

PHYSICAL PROPERTIES AND KINETICS OF  
CERTAIN REACTIONS OF THE ISOMERS  
OF ALLO-OCIMENE

By  
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## CHAPTER I

### INTRODUCTION

Allyl-acrylate, 2,6-dimethyl-2,4,7-octatriene, was first detected in acrylate and was thought to be its dimerization. Acrylate is a natural product, and has been reported in the literature as 2,6-dimethyl-1,3,5,7-octatriene, although it is believed in this laboratory to be 2,6-dimethyl-2,4,7-octatriene (1). Kollar (2-4) who investigated very extensively the chemical and physical properties of acrylate, observed that when this compound was heated for a few hours under an inert atmosphere, it was converted to allyl-acrylate. This last compound was first synthesized by Fischer and Leubner in 1933 (5) and later by Leubner (6).

A more plentiful source of allyl-acrylate is alpha-pinene. When alpha-pinene is thermally isomerized, either in the liquid or vapor phase, allyl-acrylate is obtained as one of several products. This reaction was studied thoroughly both in this laboratory and by other workers (7-11). The usual methods of pyrolyzing alpha-pinene have been either to seal the reactant in a vessel and heat it, or vaporize alpha-pinene and use an inert carrier gas to transport the vapor through the hot tube. Regardless of the method of isomerization, the usual

products at low temperatures and short contact times have been: condensed alpha-pinene, dipentene, monomer polymer and allyl-oxime. The yield of this last product can be as much as 40 percent. At higher temperatures and longer exposures alpha and beta pinenes are formed as well.

Baskin and co-workers (32-34) verified Rice's prediction (35) that oximes should be formed from the pyrolysis of alpha-pinene, and found that the half-life of the former is only about three minutes at 300° C. This explains why oximes were hard to detect and there is no doubt now that this work has been concluded, that it is the precursor of allyl-oxime. The structural formulas of the products of alpha-pinene pyrolysis are given in Figure 1.

Essentially the rate-distribution scheme for alpha-pinene is somewhat unusual in that it involves simultaneous and consecutive reactions. Baskin and Faglin (36) computed the rate constants for the dissociation of allyl-oxime according to the mechanism:



where A is an allyl-oxime molecule, and B is a diene molecule. For rate constant  $k_2$ , they found the frequency factor  $\nu_2^0$  in the integrated Arrhenius equation to derive



FIGURE 1. Structural Formulas of Alpha-Pinene Pyrolysis Products.

from the expected value for a decomposition reaction. Furthermore, Papaiak pointed out that a value of  $\log k$  of approximately 18, as found, would apply to a second order reaction.

Burt [10] extended Papaiak's work and studied the effect on the dissociation reaction of the addition of acid, base and antioxidant. He also determined dilatometrically the rate constants, and from his results drew some very interesting conclusions. First, it makes little difference whether  $k_d$  is calculated on the basis of a first or second order reverse process. Second, the conversion of dimer to allyl-radicals in the liquid phase appears to be a unimolecular reaction following a second order rate equation. Third, from the drift of the  $k_d$  constant in both Papaiak's and Burt's work, it would seem that the reversible dissociation was not the only reaction taking place. This is a good example of how kinetic data can be of great help in elucidating a chemical process, or in suggesting that a wrong assumption was made, or that there is insufficient evidence for any assumption at all.

A review of the physical constants (mainly refractive indices, densities and boiling points) for the so-called "pure" allyl-radicals shows considerable variation in the values of these constants. It was concluded that allyl-radicals was probably a mixture of some isomeric forms,

two of which were isolated by Smith (27). The structure of allyl-acetylene was proved by degradation (28), synthesis (27,2) and the use of Raman spectra (29). Consideration of the allyl-acetylene molecule indicates that four isomers are possible. Although it was noted that different temperatures of isomerization of alpha-pi-ene gave different allyl-acetylene isomers, no systematic work was done to find out why this occurred. It was suspected that there was a relationship between the temperature of formation of allyl-acetylene and the relative proportions of the isomers present. The investigation undertaken here was prompted by a desire to clarify the position with regard to the number of isomers that can be isolated. We wished to know what conditions favored the production of either isomer. Were two or more isomers formed simultaneously, or was one perhaps the initial product which isomerized to form the other? It was desired to prepare the isomers from a highly purified state, so that sufficiently reliable physical properties could be ascertained to characterize them.

Furthermore, as indicated above, the kinetic clues from the discrimination of allyl-acetylene indicated that the reaction was not as simple as expressed by equation 1. This conclusion is significant in the light of the results of the present work. In view of the complexity of the

reaction, the determination of the activation energy from only two temperature measurements is of doubtful value. It was found that the discrimination reaction is indeed not as simple as postulated by Fagnoli. The kinetic scheme, at least for the liquid phase, should now include not only simultaneous and consecutive reactions, but also reversible and competitive ones as well.

## CHAPTER 11

### REVIEW OF PREVIOUS STUDIES

The isomers of allyl-oximes were first isolated by Scherer in 1817 (1). More extensive work in the separation of the isomers was done by Bayfield (2, 3), Hunt (4) and Alder (5, 6). (3), who also provided some physical constants for the compounds. A summary of these constants, corrected to 30 mm Hg pressure and 20° C temperature, whenever necessary, was compiled and is given in Table 1. A correction factor of 1.3 degrees per mm was used for the boiling points in Table 1; it was calculated from the Clausius-Clapeyron equation (2). For the correction of densities Scherer's factor (3) of -0.0008 per degree C was used, while refractive indices were corrected through Bayly's factor (3) of -.0005 per degree C. As will be observed from Table 1, there seems to be a correlation between the temperature of pyrolysis of allyl-oximes and the occurrence of a particular isomeric form. It may be tentatively concluded that the higher the temperature of pyrolysis, the greater the amount of isomer 3 or allyl-oxime.

As mentioned in the introductory discussion, four geometrical stereoisomers of allyl-oximes are possible. These are given in Figure 1. Although methods for

TABLE I

RED: IRIDIUM CHROMIUM REACTION IN THE LITERATURE FOR ALKYL-ACETONE IRRADIATION

| No.          | Year | Irradiation System   | Boiling Point at 1 atm | $\rho_0$         | Density at 1 atm   | $G, \%$                  |            | Notes                       | Ref. |
|--------------|------|----------------------|------------------------|------------------|--------------------|--------------------------|------------|-----------------------------|------|
|              |      |                      |                        |                  |                    | Red.                     | Acet. loss |                             |      |
| 1            | 1944 | A                    | 50° C                  | 1.8400           | 0.805 <sup>a</sup> | -                        | -          | Alpha-irradiation at 200° C | 30   |
| 2            | 1944 | B                    | 51° C                  | 1.8400           | 0.805 <sup>b</sup> | -                        | -          | Alpha-irradiation at 200° C | 30   |
| 3            | 1955 | A                    | 50° C                  | 1.8410           | 0.805 <sup>b</sup> | -                        | -          | Alpha-irradiation at 200° C | 37   |
| 4            | 1955 | B                    | 51° C                  | 1.8400           | 0.805 <sup>b</sup> | -                        | -          | Alpha-irradiation at 200° C | 37   |
| 5            | 1957 | Allyl-<br>acetylene  | 55-57° C               | 1.8410           | 0.805 <sup>b</sup> | 270                      | 500        | Alpha-irradiation at 200° C | 31   |
| 6            | 1958 | 99.999-<br>refluxant | 16.2° C                | 1.7613           | 0.811 <sup>b</sup> | 270                      | 270        | Alpha-irradiation at 200° C | 31   |
| (a) $\rho_0$ |      | (b) Vapor phase      |                        | (c) Liquid phase |                    | (d) $G_{\text{acetone}}$ |            |                             |      |



FORM I: Trans-C-4,5, Trans-C-6,7



FORM II: Trans-C-4,5, Cis-C-6,7



FORM III: Cis-C-4,5, Cis-C-6,7



FORM IV: Cis-C-4,5, Trans-C-6,7

FIGURE 6. Stereoisomers of Ata-rubbers.

assigning absolute gig or hogg configurations to isomers of an elastic compound are rather doubtful (28), it is found that the gig isomer usually has the lower boiling point, higher boiling point and higher density. On the basis of these considerations and the Raman spectra for the two forms of cis-octamers, Seyfield gig gig. (29) decided to assign the hogg-C<sub>8</sub>-hogg-C<sub>8</sub> configuration to form I, and the hogg-C<sub>8</sub>-gig-C<sub>8</sub> configuration to form II (Figure 3).

After gig gig, (28) attacked the problem through a different method. By synthesizing two isomeric diacids, C<sub>14</sub>H<sub>28</sub>O<sub>4</sub>, derived from the two isomers they had prepared, they proved that the form with the lower boiling point and lower density had a hogg-C-4,4, hogg-C-4,7 configuration, while the form with the greater density and higher boiling point had a hogg-C-4,4, gig-C-4,7 configuration. These conclusions corroborate Seyfield's work.

Small (30) claimed to have isolated a third isomer, in addition to the two described above. Fortunately a sample of the "third" isomer was available when this work was started. A gas chromatographic analysis showed it to be purely a mixture of the A and B forms. The infrared evidence for the existence of a third isomer is also unconvincing.

A source of considerable difficulty in the study of silicic acid is the fact that it absorbs oxygen so rapidly. Unless very stringent precautions are taken to avoid oxygen contamination, some kind of polymer oxide is formed which will change the constants, even though the samples were very pure to begin with. The oxidation of silicic acid was studied by Trumbull (10) who postulated the following steps for the reaction: (a) vigorous addition of oxygen, accompanied by (b) much polymerization followed by (c) some autocatalytic polymerization. The pathway used that forms when silicic acid is left in an open flask exposed to the air, is believed to be an unstable polymer oxide  $(\text{Si}_2\text{O}_5)_n$ . It was found in this laboratory that the polymer material could be dissolved only by reducing alkalis; the other common solvents were ineffective.

## CHAPTER III

### EXPERIMENTAL

The two most convenient methods of preparing large amounts of allyl-ethers are (a) vapor phase pyrolysis and (b) liquid phase pyrolysis of alpha-glucose. Preliminary experimental work in these two methods indicated that, provided alpha-glucose had the best physical constants reported in the literature, and was chromatographically pure, the results were identical whether sulfuric glucose or acid glucose was used.

#### Fractionation Apparatus

Unfortunately, none of the excellent Lesty and Swell type rectification columns, constructed and tested in this laboratory a few years ago (17), was available when this work was started. Therefore, new fractionation systems had to be built and tested. One that was found satisfactory for the purification of alpha-glucose and the separation of pyrolysis products and isomers is described below.

The column was 180 cm long (measured from top to bottom of packing), 2.5 cm inside diameter, filled with Poropak P packing, purchased from the Scientific Development Co., State College, Pa. The column was placed

in a heat-compensating jacket (20), and the two-section silicone heaters were regulated with two Potentiostat variable transformers. The column used to separate the two isomeric forms of allyl-silicone was one identical to that just described, but 150 cm long.

A very efficient distilling head was constructed incorporating the following features: (1) A very effective condenser which, properly cooled, prevented vapor from escaping to other parts of the system. (2) A magnetically operated funnel permitted precise reflux-ratio control. (3) All components in the path of the distillate (with the exception of a helium seal) were eliminated to avoid grease contamination.

A reliable electronic repeat cycle timer, manufactured by the E. O. Wilson & Co., Burlington, V. Pa., was used to regulate the take-off speed. The cooling of the distilling head was effected by means of a pump circulating water at about 12° C from a refrigerated reservoir. The absolute pressure in the fractionating system was measured by means of a precision model Timmerli gauge. The pressure could be read directly as the vacuum scale is 1/100th of a millimeter.

A modified Baranovsky and Kozlovsky type manual (21) was used to control the pressure to  $\pm .1$  to 1 g. Hydroplene gased with a very small amount of helium chloride was used

in the absence of sulfuric acid. This necessitated building a very sensitive electronic relay. A further innovation was the use of dry, oxygen-free nitrogen instead of air. This was introduced through a valve (usually closed) purchased from the Inconel Valve Co., Flushing Park, N. J. (series 305, #25034-0000). When pressure decreased, the relay operated the valve which admitted, through a capillary tube, enough nitrogen to restore pressure. This produced a slight, continuous fluctuation in pressure which increased the efficiency of the column.

The temperature of the head, still and column was recorded continuously and continuously by thermocouples connected to a multiple-printing Brown Electrode, Minneapolis-Omagueli 0-100° C recorder. This method was extremely convenient, as it not only provided a permanent record of the boiling point, pot and column temperatures, but also furnished a warning in case of accidental temperature or pressure changes.

The column efficiency was determined by refluxing a mixture of n-heptane and methyl cyclohexane in the column at atmospheric pressure until equilibrium was established. Two very small samples were then taken, one from the head and the other from the distillation flask. The refractive indices of these samples were measured, and the number of

plates was determined directly from a plot of number of plates versus refractive index of mixture (48). The 1.4 meter column had an efficiency of about 45 plates, while that of the 1.8 meter was about 60 plates.

The distillation system was operated in accordance with standard procedures (36, 49), but a certain amount of experience was necessary to obtain good results.

Three difficulties were encountered in connection with the prolonged operation of the distillation system. The first was in connection with finding a suitable taper grease that would be impervious to toluene vapors and maintain a vacuum tight seal over an indefinite period of time at low pressures and temperatures of about  $100^{\circ}\text{C}$ . Different kinds of commercial taper greases were used, but they all proved unsatisfactory, particularly at points where liquid or hot vapor came into contact with the seal. Teflon taper sleeves were tried, but they developed fine channels at low pressure, with subsequent leaks. Finally, a type of grease was developed which proved completely reliable. Two parts of dextrin to one part of d-mannitol were mixed with enough acetone (or some other inert solvent) to form a fairly viscous suspension. To use, the mixture was quickly smeared on to the lower part of the male taper, immediately bringing the female joint in place and rotating to produce an even distribution of the material.

The joint was uniformly and very carefully heated with a gas stirrerburner, until the hydrosulfuric barely melted; the female taper was then rotated. This grease provided an excellent seal that was not affected by nitrogen vapors or liquids for any period of time. To break the seal, the joint was again heated, very carefully, with the stirrerburner until the grease began to melt; a sharp twist of the female taper loosened the joint. Extreme caution must be exercised to avoid burning the hydrosulfuric mixture by excessively heating the glass joints. If this should happen, the grease turns brown, and the tapered can only be taken apart by breaking.

The second difficulty was experienced in attempting to prevent the solid traps from clogging and freezing, thus stopping the distillation. The problem was solved by using three solid traps in two large capacity dewar flasks filled with a dry ice-acetone mixture. A system of stopcocks was used to by-pass and clean any particular trap, without disturbing the pressure equilibrium. This is shown in Figure 1.

The third difficulty was in connection with fraction collection. In view of the fact that small samples of distillate were continuously taken and analyzed, it was



(a)



(b)



(c)

FIGURE 2. Distillation System. (a) By-Pass Cold Traps. (b) Fraction Collector. (c) Flow-off Regulator.

designed to have a collector that would permit this without disturbing the equilibrium. Such a collector was built and proved very successful; it is shown in Figure 3.

The whole system was connected to a pressure operated "fail-safe" device used when the distillation was unattended. If, due to power failure or other cause, the pressure changed by about as little as  $\pm 5$  mm the mercury in a U-tube with three contacts activated a master relay that turned off all power. The relay could be reset only manually, so that even if power was restored, the system would remain inoperative. This regulator is shown in Figure 4.

### Gas Chromatography

Vapor phase chromatography proved an invaluable tool in the qualitative analysis of pyrolysis products, in following the course of distillations and in the quantitative determinations of the isomers. A commercial vapor fractionator was used, the Porapak-Qmar Model 104B. Considerable experimentation was needed to find a chromatographic column that could separate all the components of the pyrolysis mixture and also resolve the isomers. Columns of from 4 to 40 feet long were constructed and tested. The solid supports were mostly diatomaceous earth products manufactured

by Johns-Manville Co., such as Chromosorb W, 40-100 mesh. The stationary liquid phases were various high boiling materials, such as silicone oil, Carbowax 4000 and 6000, di-(2-ethyl hexyl) phthalate, diethyl phthalate, di-n-octyl sebacate and others. A 40-foot column packed with special synthetic detergent granules (F & S Tides) gave an almost complete separation of the isomers, but could not be used for quantitative work due to irreversible absorption.

The column that was used for most of the chromatographic work, including quantitative determinations in the kinetic studies, was a stainless steel one, 4 feet long, with di-n-octyl phthalate as the liquid phase. All of the gas chromatographic columns were taken 1/4 inch in outside diameter and 1/16 inch in inside diameter. The long columns were constructed of either copper or aluminum tubing, while the short ones were of stainless steel tubing.

#### Purification of Alpha-Pinene

Alpha-pinene (99%), about 95 percent pure, was obtained from the Glidden Co., of Jacksonville. It was purified in batches of about five liters, by fractional distillation. The purity was checked by means of refractive index, density and gas chromatography. A large volume of

very pure alpha-placon was collected and stored under dry, oxygen-free nitrogen. It had the following constants: boiling point (80.0 mm)  $88^{\circ}\text{C}$ ;  $n_D^{20}$  1.4533;  $d_4^{20}$  .862.

#### Vapor Phase Isomerization of Alpha-Placon

Apparatus. The vapor phase pyrolysis of alpha-placon was effected by means of a special column, shown in Figure 4. The column was insulated and the jacket could be maintained to  $\pm 5^{\circ}\text{F}$  at a pre-set temperature by using a thermocouple-controlled pyrocontrol (Honeywell, Brown Py-B-3-5000). The pot was off-set to prevent back flow and re-spilling of reactant and products, and was heated to about  $150^{\circ}\text{C}$ . The reactant vapor was swept through the pyrolysis tube by means of a constant flow of dry, oxygen-free nitrogen. To measure accurately the flow of gas, a rotameter (Fro-lapier, 4-11-B, low-flow) was installed and calibrated. Nitrogen flow was maintained at 200 cc/minute, and the gas was dispersed in the liquid through a fritted glass cylinder. Above pre-purified nitrogen was used, and traces of oxygen were removed by passing the gas through a glass tube, filled with fine copper filings, thoroughly cleaned and heated to about  $350^{\circ}\text{C}$ .

Procedure. A 300 ml portion of pure alpha-placon was placed in the pot, care being taken to exclude oxygen,

# FIGURE 4

- 1 Pyrex Glass Tube .001 inch i.d. 122 cm long
- 2 Insulation Around Tube
- 3 Pyrex Glass Tube 7.5 cm o.d.
- 4 Aluminum Foil Insulation
- 5 Insulation Insulation
- 6 Aluminum Support
- 7 Pyrex Glass Inner Tube 3 cm i.d.
- 8 Aluminum Support
- 9 Pyrex Glass Tube Spacer, Sealed at Both Ends,  
.010 inch o.d. 60 cm long. Tube just fits  
Pyrex Glass Tube.
- 10 Pyrex Glass Glass Seal
- 11 Pyrex Glass Glass Seal
- 12 Aluminum Support
- 13 24/40 ST
- 14 Tube
- 15 Thermometer Well
- 16 Fitted Gas-Dispersion Tube
- 17 Roundhead Flask
- 18 Gas Inlet
- 19 24/40 ST
- 20 24/40 Adapter
- 21 Copper-Catalyzed Thermocouple
- 22 Thermocouple Well
- 23 Heater Leads to Controller
- 24 Sealed
- 25 Heater Leads to Controller
- 26 Thermocouple Leads
- 27 24/40 ST
- 28 Minneapolis-Maryland from Pyrex  
Temperature Controller and Relay
- 29 To Two Pyrex Glass Condensers and Sample Collector

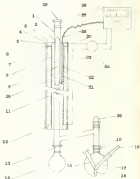


FIGURE 4. Apparatus for Vapor Phase Pyrolysis of Alpha-Pinene.

The nitrogen was allowed to bubble through while the pot and column temperatures came up to the desired value. The white vapor of alpha-pyrene and products was carried through two Friedrichs condensers. The vapor that condensed and was collected during the warm-up period or between temperature settings was discarded. Forty ml. samples were collected at each reaction temperature.

Identification of Products. The samples were analyzed by gas chromatography, using the di-ter-decyl phthalate, 4-foot column. Six components were detected: unreacted alpha-pyrene, dipicene, valene, allyl-valene, alpha and beta pyrenenes. For typical runs Figure 1 shows the effect of temperature of pyrolysis on the products formed. At low temperatures, only valene and dipicene are formed. At higher temperatures, valene, dipicene and allyl-valene are formed. Finally, at very high temperatures, dipicene, allyl-valene and pyrenenes are formed. In high-boiling components, such as allyl-valene dimers were detected at any temperature. The analysis for high-boiling components was carried out by gas chromatography using a silicong oil column at 300° C. At this point it is interesting to note that only two isomers of allyl-valene are produced, and that one isomer

Approximate Retention Times. Alpha-Fluorene: 3.8 minutes, Benzene: 8 minutes, Diphenyl: 9.3 minutes, Alfa-acetone A: 9.8 minutes. Alfa-acetone B: 10.8 minutes. Pyrene: 11.5 minutes.

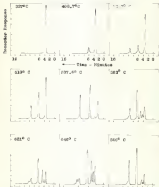


FIGURE 5. Chromatograms Showing the Effect of Temperature on the Super-Phase Synopsys of Alpha-Fluorene.

is predominant at low temperatures, while more and more of the other isomer appears as the pyrolysis temperature is increased.

### Liquid-Phase Polymerization of Alpha-Pinene

Apparatus: Isolated Reaction Setup. Pyrex round glass tubes 3.25 cm outside diameter, 1.45 cm inside diameter, 125 cm long were sealed off and rounded at one end, while the other end was fire-polished. The tubes were first placed in an annealing oven to burn off any organic material, and then a strong stream of nitrogen was blown in (using a 6-inch spring nozzle). Then the tubes were effectively cleaned and filled with nitrogen by blowing out the air and capping with a rubber cover.

The tubes were filled with 1/10th M alpha-pinene, under a nitrogen blanket. Each filled tube was connected to a vacuum line at 6-1 mm, through a cold trap and a 500 ml flask. The tube was first connected to a CO rubber stopper, which in turn was attached to a flexible heavy gauge rubber tubing which led to the flask. A two-way stopcock between the cold-trap and flask was used either to exhaust or admit air. Both the flask and the tube were evacuated at the same time, gradually, and this prevented the contents from being oxidized etc. As soon

as the tube was completely evacuated (as indicated by the U-tube gauges) it was sealed by collapsing the wall, about 1 cm above the surface of the liquid with an oxygen torch.

Air-bath. The filled tubes were reacted in a Tamm oven thermostated by a Minneapolis-Dewey controller.

Identification of Products. The same products were observed in the liquid phase pyrolysis as in the vapor phase pyrolysis, with the exception that high boiling components were formed even at low temperatures.

The precaution was always taken to break an evacuated sealed tube and analyze its contents, to ensure that the sealing process did not form any products. The effect of the temperature on alpha-piensa in sealed tubes in the liquid phase, for typical runs, is shown in Figure 4.

Summary. In 1959, Beckman and Harris (41) claimed to have prepared alpha-piensa by the vapor phase isomerization of alpha-piensa. Further work in this laboratory by another investigator showed that this method was difficult, and results hard to reproduce.

The relatively simple operation for the vapor phase isomerization of alpha-piensa described in this chapter, affords a very convenient means of preparing large quantities

Approximate Retention Times. Alpha-Tinene: 3.8 minutes, Bismene: 8 minutes, Pimene: 8.8 minutes, 4,8a-dimethyl-4: 8.8 minutes. 4,11a-dimethyl-8: 10.2 minutes. Pymene: 4-6 minutes.

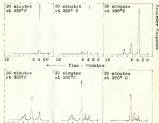


FIGURE 4. Chromatograms Showing the Effect of Temperature on the Liquid-Phase Pyrolysis of Alpha-Tinene.

of acetone. It will be observed from Figure 2 that acetone is produced at the following temperatures:  $400^{\circ}$  and  $500^{\circ}$  C. The residence time of acetone, the precursor of allyl-acetone in the pyrolysis column is very small, and in spite of the short half-life of acetone at high temperatures, some of it survives and can be isolated. However, the study of acetone is beyond the scope of this work.

## CHAPTER IV

### PREPARATION AND PURIFICATION OF ALKO-ACETONE ISOMERS

After a thorough investigation of the conditions which produced alko-acetone from the liquid and vapor phase pyrolysis of alpha-pinene, it could be concluded that only two isomers were formed. Several samples of the linear alkenes were forwarded to other laboratories for analysis, and it was reported, without exception, that only two components could be detected and resolved. The samples were sent to the Glidden Co., Johnstonville, Utah; Charles; Van Ameringen-Bastler Inc., N. Y.; and the Permutin Powder Co. The analyses were mainly chromatographic and spectroscopic. Dr. E. Hunt of the Glidden Co., performed analyses by gas chromatography using 100-foot long capillary columns, ordinary columns with different liquid phases, and temperature programming.

Some further conclusive evidence that only two isomers appear under the special conditions of preparation described in the previous chapter, is the fact that there exists a one-to-one correspondence between physical properties and chromatograms. In the course of separating the isomers by distillation, whenever the chromatograms showed one peak only, representing one isomer, the refractive index, density and infrared spectra remained unchanged. The refractive

index does not appear to be the best criterion with regard to purity of the isomers, the reason being that allyl-azulene is very sensitive to oxygen contamination. Even a short exposure to air produces an appreciable change in the refractive index. This fact and the incomplete separation of the two isomers may be responsible for the variation in the constants for the two isomers. However, provided the compounds are chromatographically pure, it was found that the values are reproducible if care is taken to exclude oxygen. The precautions must go as far as filling a flask with nitrogen prior to introducing the pure liquids, or returning a solvent with nitrogen before using it to make a solution. In a very dilute solution, the dissolved oxygen reacts with allyl-azulene altering the concentration. This fact was observed in dielectric constant measurements.

The vapor phase pyrolysis of alpha-vinylene was chosen as the most convenient method of preparing the isomers. Large quantities of the reactant could be pyrolyzed with ease at a pre-determined temperature, and the yield was good. The liquid phase pyrolysis is not desirable because a side reaction, polymerization, reduces the isomers, reducing the yield.

The carefully purified alpha-phenene was pyrolyzed in five-liter batches in the apparatus already described. Although at low temperatures this method gives one isomer

from exclusively, a temperature was chosen that would produce both forms in the proportion of 3:8. This procedure was adopted since the higher boiling form could not be formed by itself from alpha-phase under any circumstances. Mixtures of the two isomers, approximately equimolar, could not be separated with the most efficient column, but a mixture with about 50 percent or more of either component could give a small amount of both forms in very pure state.

The short distillation column was used to strip the unreacted alpha-phase and diene from the precipitate products, leaving a mixture of the two isomers. About five liters of this mixture was collected from successive precipitate runs. The long fractionation column was used to separate a small amount of the two isomers in the five-liter mixture. This last distillation was very close, its fraction being about nine parts. From the five liters of the mixture, about 400 ml of one isomer and about 300 ml of the other were isolated.

The purity of each isomer was 95 percent, the 3 percent being the other form (determined chromatographically). Further purification was attempted by fractional freezing. Special apparatus was built for this purpose, and is shown in Figure 7. The double-walled container was surrounded in a dry ice-acetone mixture, and the material was cooled

FIGURE 7

- 1 300-Hech Stainless Steel Valve
- 2 150-Hech Stainless Steel Valve
- 3 Nitrogen Gas Inlets
- 4 22/70 RT
- 5 Thermocouple Opening
- 6 Stirrer Opening
- 7 18/24 RT
- 8 Pyrex Brand Glass Tubing, 20.8 x 5 mm
- 9 Stirrer
- 10 Pyrex Brand Glass Tubing, 12 x 4 mm
- 11 Pyrex Brand Glass Tubing, 20 mm

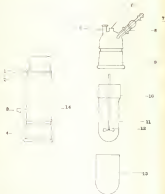


FIGURE 9. Fractional Crystallization Apparatus.

slowly, with mechanical agitation. When about more than half of the material crystallized (fine white crystals), the liquid phase was removed. Flowing nitrogen provided a continuous blanket at all times over the liquid to prevent moisture condensation and oxygen condensation. Each form was subjected to this final purification, giving a product 99 percent pure. The highly purified isomers were kept in specially constructed flasks with ground-glass joints, the main joint being part of the flask. This prevented the vapor pressure from getting into the liquid.

## CHAPTER V

### PHYSICAL PROPERTIES OF ALLO-OCIMENE

#### Boiling Points

The boiling points of the two isomers were determined by an extrapolation of the plateaus in the plots of the vapor temperature versus the volume percent distilled in a distillation of the pure compounds. The temperature was recorded with the known Beckmann thermometer mentioned before, using thermocouples in a silicone oil bath at the distilling head. The recorder was calibrated at the ice-point and boiling point of water, 20.0°C (freezing point 20.0° C), and at other points using a National Bureau of Standards thermometer. The pressure was maintained at 760 mm  $\pm$  .2 mm with the regulator already described. The boiling points were as follows: Form A, 88.0° C; Form B, 81.0° C.

#### Refractive Index

The refractive index of each form was determined with a Bausch and Lomb Abbe-type refractometer. The temperature was kept at 20.0°  $\pm$  .05° C by circulating water from a constant temperature bath. Temperature variations were noted with a Beckman differential thermometer. A National Bureau of Standards thermometer

was used to record the temperature of the bath. Lens A had a refractive index of 1.5415, and lens B had a value of 1.5448. The refractive indices were also determined at  $20.0^{\circ}\text{C} \pm .00^{\circ}\text{C}$  and were: Lens A: 1.5448; Lens B: 1.5420.

### Sampling

The usual pycnometer with capillary necks were unsatisfactory for very accurate density determinations. A lipid type (42) pycnometer was found very useful, and all determinations were made with it. Several pycnometers of this type were purchased from the Lee Glass Co., Cincinnati, N. J. The advantage of this pycnometer is that loss by evaporation is avoided due to the slow rate of diffusion through the partially filled capillary arms. The area of exposure to vapor is also negligible, especially if the open ends of the capillaries are blanketed in nitrogen, as they were. A small change that was made on the pycnometer was to slant the neck on the filling side by attaching a 5 cm long capillary. This permitted an easier filling of the bulb when the capillary was dipped into the liquid. The pycnometer filled fairly rapidly when dilute solutions were used, but a suction bulb was needed for more viscous pure compounds.

The pycnometer used in these determinations was calibrated with freshly distilled water free from air, and was then checked with very pure benzene. It had a capacity of about 10 ml. The calibrations were carried out at 20° C and 25° C. The pycnometer was calibrated by obtaining the volume at 20° C and 25° C of water (freshly distilled, free from air) at different points on the scale of the pycnometer. At 20° C the volume was calculated by dividing the weight of water by .99823 (44), while at 25° C the volume was found by dividing by .99707 (44). Calibration curves were then drawn, plotting the sum of the scale divisions on both arms as the abscissa, and the volume in milliliters as the ordinate. The calibration data are given in Table 3, while the calibration curves for the pycnometer at the two temperatures are given in Figure 5. However, in order to read the volume to four decimal places, the curves actually used were plotted on cross section millimeter coordinate paper of one square-meter size.

A sealed counterpoise was used to compensate for buoyancy of the air. A correction factor of  $[-\text{vol} \times (1-\rho_a)]$  (43) was added to the observed density at 20° C to correct all weights to vacuum, where  $\rho_a$  is the density in air. At



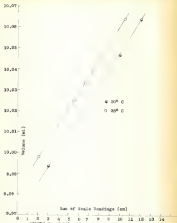


FIGURE 8. Calibration of Thermometer.

$10^6$  & the weights were corrected to vacuum by using the

$$W = W^1(1.0013) \quad T-1$$

equation where  $W$  is the weight in vacuum, and  $W^1$  is the weight on the pan.

Check points on the water calibrations were made with very pure benzene. The densities of benzene at 20.0 and 20.5° C agreed with the values of .6799 and .6797 respectively, reported by Timmermans (48).

The densities of the two isomers at 20.0° were as follows: Para A, .8097; Para B, .8115. At 20° C the values were: Para A, .8085; Para B, .8071.

### Dielectric Constants

The dielectric constant,  $\epsilon$ , of a substance is defined as the ratio of the capacitance,  $C$ , of a condenser filled with the material between the plates, to that  $C_0$ , of the condenser with a vacuum between the plates. Thus the determination of dielectric constants consists in capacitance measurements and the Schering Bridge method (49) was used for this purpose. The bridge was a General Radio Company Type T10-A, consisting of a measuring cell and a precision capacitor. The power source for the bridge was a General Radio Company Type 1202-A oscillator. The measurements were made at two frequencies: 50 and 60 kc. The balance of the bridge was detected with a Tektronix Type 541-A oscilloscope.

The capacitance cell used, model 2120, was manufactured by Balough Laboratories, Norwalk, Conn. Throughout the measurements it was kept in a constant temperature bath held to within  $\pm .01^\circ \text{C}$  of the preset temperature.

The total capacity of a cell can be expressed by the following relation:

$$C = \epsilon C_0 + C_1 \quad (7-2)$$

where  $C$  is the total measured capacitance,  $C_0$  is the replaceable capacitance,  $C_1$  is the residual capacitance, and  $\epsilon$  is the dielectric constant of the material in the cell.

A standardization was performed with air and very pure benzene, and the constants in the above equation were thus determined. The calibrations at  $20^\circ$  and  $30^\circ \text{C}$  were checked with pure carbon tetrachloride for which the dielectric constants found were 2.2433 and 2.2314 respectively. The literature values (45) are 2.2433 and 2.2317. The values of  $\epsilon$  used for pure benzene were 2.2822 and 2.2758 (46).

The physical constants of the solvents used were determined and found to be as follows: Benzene at  $20^\circ \text{C}$ ,  $d=0.8786$ ,  $n_D^{20}$  1.5011; at  $30^\circ \text{C}$ ,  $d=0.8707$ ,  $n_D^{30}$  1.5079. Carbon tetrachloride at  $20^\circ \text{C}$ ,  $d=1.5942$ ,  $n_D^{20}$  1.4602; at  $30^\circ \text{C}$ ,

$\delta=1.4880$ ,  $n_D=1.4973$ . These values are in close agreement with those reported by other investigators.

Instead of using equations 7-3, with the evaluated constants at each temperature, the following equations were used to calculate  $n$  directly from the experimental measurements.

At 20°C. C:

$$n = 1 + (1.4880) \left( \frac{C^2}{n^2 - 1} - \frac{C}{n} \right) \quad 7-5$$

At 25°C. C:

$$n = 1 + (1.4973) \left( \frac{C^2}{n^2 - 1} - \frac{C}{n} \right) \quad 7-6$$

where  $C^2$  is the capacity with the airtorial in the cell,  $C$  is the capacity with nitrogen in the cell, and  $C^0$  is the capacity with benzene in the cell. The two equations are derived from relation 7-3 by solving simultaneously the equations with nitrogen in the cell and with benzene ( $n=1.4973$  and  $n=1.4880$  respectively at the two temperatures) in the cell.

The cell was thoroughly cleaned with absolute ethanol, acetone and then dried over a benzene burner before each run. It was cooled under a stream of nitrogen to avoid solvents condensing on the inside walls. All transfers of liquids were made under a blanket of nitrogen to prevent oxygen contamination. The top of the neck of the cell

was slightly greased with talc-free grease to ensure an air-tight connection after about 20 ml of liquid had been pipetted in it and nitrogen blown gently over the solution. The advantage of the talc-free grease is that it can be removed easily and completely with acetone.

The dielectric constants for the two pure isomeric forms of allyl-acetylenes were calculated. The values at 20° C are: Isomer A, 2.8148; Isomer B, 2.8786. At 30° C the values are: Form A, 2.8071; Form B, 2.8688.

### Dipole Moments

The dipole moment is an important structural characteristic of a molecule. For the isomers the dipole moments were calculated at two temperatures from the dielectric constants and other data of dilute solutions in a nonpolar solvent.

Preparation of solutions. The solutions were prepared by weight. All transfers were made under nitrogen to exclude oxygen, small traces of which interfered with measurements. When this precaution was not observed, results in dielectric constant determinations were inconsistent. However, when care was taken to exclude the benzene used in the solutions with nitrogen, to exclude air from the cell, and to discard each used portion of the

solution, the results were consistent and reproducible. Likewise considerable scattering of experimental points occurred. The data on the solutions are given in Table 2.

Densities of the solutions. The data for density determinations are given in Tables 4 and 5. In the same tables will be found the refractive indices of the solutions. All weights were corrected, and the same procedure was followed as outlined before. Each portion of a solution that was used in density determinations was discarded.

Dielectric constants and refractive indices of the solutions were obtained as mentioned in previous sections. The dielectric constants of the solutions for the two isomers at the temperatures are given also in Tables 4 and 5.

Method of Finding Data. The usual procedure in finding dipole moments from data on dilute solutions is the extrapolation of the polarizations. The method used here is a direct mathematical extrapolation of the dielectric constant and density data. Benetstrand (42) assumed that in dilute solutions the dielectric constants and densities are linear functions of the mole fraction. That is, the following relations hold:

$$\epsilon_{12} = \epsilon_2(1 + \alpha x_2) \quad \text{Eq. 6}$$

$$\rho_{12} = \rho_2(1 + \beta x_2) \quad \text{Eq. 7}$$

TABLE 3

DATA ON SOLUTIONS FOR SINGLE MONOMER SUBSTITUTION

| Solution No. | Weight in Grams |         | Mole Fraction |         |
|--------------|-----------------|---------|---------------|---------|
|              | Isomer A        | Residue | Isomer A      | Residue |
| 1-A-2        | .7714           | 42.7512 | .0000         | .0000   |
| 2-A-2        | 1.5070          | 42.7542 | .0000         | .0760   |
| 3-A-2        | 2.2214          | 42.7407 | .0004         | .0760   |
| 4-A-2        | 2.9358          | 42.8317 | .0408         | .0804   |
| 5-A-2        | 4.6502          | 42.8307 | .0400         | .0808   |

| Solution No. | Weight in Grams |         | Mole Fraction |         |
|--------------|-----------------|---------|---------------|---------|
|              | Isomer B        | Residue | Isomer B      | Residue |
| 1-B-2        | .7664           | 42.7602 | .0000         | .0000   |
| 2-B-2        | 1.5042          | 42.7602 | .0000         | .0764   |
| 3-B-2        | 2.2187          | 42.7403 | .0007         | .0802   |
| 4-B-2        | 2.9372          | 42.7509 | .0402         | .0802   |
| 5-B-2        | 4.6557          | 42.7540 | .0408         | .0804   |

Table 4

DATA FOR DIRECT WEIGHT MEASUREMENTS AT 90° C

| Compound<br>or<br>Solubility | Re-<br>fractive<br>Index | Disper-<br>sion<br>Coefficient | Density | Values of<br>Solubility<br>at<br>90° C |                   |
|------------------------------|--------------------------|--------------------------------|---------|----------------------------------------|-------------------|
|                              |                          |                                |         | Weight<br>Percent                      | Volume<br>Percent |
| Benzene                      | 1.4918                   | 0.0028                         | 0.699   | 0.1000                                 | 0.1000            |
| Toluene                      | 1.4940                   | 0.0140                         | 0.867   | 0.4007                                 | 0.4007            |
| Trinitro-<br>Toluene         | 1.4920                   | 0.0195                         | 0.113   | 0.000                                  | 0.000             |
| 1-1-2                        | 1.4911                   | 0.0030                         | 0.892   | 0.1004                                 | 0.1004            |
| 2-2-2                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 3-3-3                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 4-4-2                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 5-5-2                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 6-6-2                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 7-7-2                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 8-8-2                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 9-9-2                        | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 10-10-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 11-11-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 12-12-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 13-13-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 14-14-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 15-15-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 16-16-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 17-17-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 18-18-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 19-19-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |
| 20-20-2                      | 1.4900                   | 0.0030                         | 0.890   | 0.1000                                 | 0.1000            |

TABLE 9  
DATA FOR STEADY-STATE TEMPERATURES AT 20° C

| Data for Steady-State Temperatures |                           |                             |          |                                 |                     |
|------------------------------------|---------------------------|-----------------------------|----------|---------------------------------|---------------------|
| Compound<br>in<br>Solution         | Free-<br>Energy<br>Factor | Disso-<br>ciant<br>Constant | Based by | Prima-                          | Ref. in State       |
|                                    |                           |                             |          | ry--<br>Solution or<br>Compound | Ref. in<br>Compound |
| Benzene                            | 1.4078                    | 1.4078                      | 1.4078   | 1.4078                          | 1.4078              |
| Acetone                            | 1.4081                    | 1.4081                      | 1.4081   | 1.4081                          | 1.4081              |
| Acetone                            | 1.4082                    | 1.4082                      | 1.4082   | 1.4082                          | 1.4082              |
| 1-4-2                              | 1.4084                    | 1.4084                      | 1.4084   | 1.4084                          | 1.4084              |
| 1-4-2                              | 1.4085                    | 1.4085                      | 1.4085   | 1.4085                          | 1.4085              |
| 1-4-2                              | 1.4086                    | 1.4086                      | 1.4086   | 1.4086                          | 1.4086              |
| 1-4-2                              | 1.4087                    | 1.4087                      | 1.4087   | 1.4087                          | 1.4087              |
| 1-4-2                              | 1.4088                    | 1.4088                      | 1.4088   | 1.4088                          | 1.4088              |
| 1-4-2                              | 1.4089                    | 1.4089                      | 1.4089   | 1.4089                          | 1.4089              |
| 1-4-2                              | 1.4090                    | 1.4090                      | 1.4090   | 1.4090                          | 1.4090              |
| 1-4-2                              | 1.4091                    | 1.4091                      | 1.4091   | 1.4091                          | 1.4091              |
| 1-4-2                              | 1.4092                    | 1.4092                      | 1.4092   | 1.4092                          | 1.4092              |
| 1-4-2                              | 1.4093                    | 1.4093                      | 1.4093   | 1.4093                          | 1.4093              |
| 1-4-2                              | 1.4094                    | 1.4094                      | 1.4094   | 1.4094                          | 1.4094              |
| 1-4-2                              | 1.4095                    | 1.4095                      | 1.4095   | 1.4095                          | 1.4095              |
| 1-4-2                              | 1.4096                    | 1.4096                      | 1.4096   | 1.4096                          | 1.4096              |
| 1-4-2                              | 1.4097                    | 1.4097                      | 1.4097   | 1.4097                          | 1.4097              |
| 1-4-2                              | 1.4098                    | 1.4098                      | 1.4098   | 1.4098                          | 1.4098              |
| 1-4-2                              | 1.4099                    | 1.4099                      | 1.4099   | 1.4099                          | 1.4099              |
| 1-4-2                              | 1.4100                    | 1.4100                      | 1.4100   | 1.4100                          | 1.4100              |

where the subscripts 1, 2, 12 refer to the pure solvent, solute and solution respectively,  $x$  is the mole fraction, and  $\alpha$  and  $\beta$  are constants. The values calculated for the constants  $\alpha$  and  $\beta$  from the mathematical extrapolation of density and dielectric constant data are given in Table 3 below.

TABLE 3  
VALUES OF CONSTANTS  $\alpha$  AND  $\beta$

| Compound | Temperature<br>$t_C$ | $\alpha$ | $\beta$ |
|----------|----------------------|----------|---------|
| Isomer A | 30                   | .3336    | -.1777  |
| Isomer A | 50                   | .3376    | -.1767  |
| Isomer B | 30                   | .2730    | -.1976  |
| Isomer B | 50                   | .3178    | -.1753  |

That equations 7-9 and 7-6 hold is seen from a few typical plots in Figures 8-10.

The solar polarization of the solute at infinite dilution was obtained by using a slightly modified version of a relation originally derived by Subramanian and Foster [48].

$$P_{2\infty} = \frac{(n_2 - 1)(n_2 + n_1\beta)}{(n_1 + 2)n_2} + \frac{2n_2 n_1 \alpha}{(n_2 + 1)^2 n_1} \quad 7-7$$

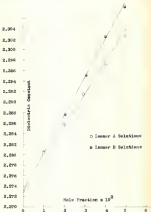


FIGURE 3. Dielectric Constant of Lower A and Lower B Solutions in Benzene.



FIGURE 10. Density of water as a function of salinity.

The dipole moment,  $\mu$ , was calculated by using the Debye equation:

$$\mu = .0183 \times 10^{-18} \left[ CP_{2,00} - \frac{1}{2}P_0 \right]^{\frac{1}{2}} \quad \text{7-8}$$

Due to solvent effects, the  $P_{2,00}$  value may be in error, affecting the dipole moment by as much as 10 percent. Furthermore, in using the Debye equation we have neglected the atomic polarizability, which is assumed to be small.

The total polarization of a substance is composed of orientation polarization, electronic polarization and atomic polarization, or

$$P = P_A + P_E + P_O = \frac{N}{V} \left( \frac{\epsilon - 1}{4\pi} \right) \left( \frac{1}{T} - \frac{1}{T_0} \right) = a + b/T \quad \text{7-9}$$

which is the abbreviated Debye equation as applied to a pure substance. The determination of the dipole moment from equation 7-9 is thus possible by obtaining a value for  $b$ . This last method was used as a rough check on the other procedure. Figure 11 gives the plot of  $P$  versus  $1/T$ .

The dipole moments were calculated by the two methods and are given in Table V.

### Infrared Spectra

The parent isomeric forms of allyl-oximes were used to obtain the infrared spectra. The spectra were determined

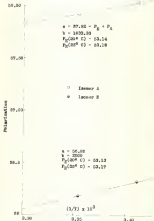


FIGURE 11. The Influence of Temperature on Polarization.

TABLE V  
SINGLE MEASURES

| Single Measure in Single Trials |                  |                      |                   |                         |
|---------------------------------|------------------|----------------------|-------------------|-------------------------|
| Tanner<br>Position              | Tempera-<br>ture | From Equation V-8    |                   |                         |
|                                 |                  | Calculated<br>Values | Average<br>Values | From<br>Equation<br>V-8 |
| 1                               | 30               | .81                  |                   |                         |
| 2                               | 30               | .80                  |                   |                         |
| 3                               | 30               | .80                  |                   |                         |
| 4                               | 30               | .84                  |                   |                         |
| 5                               |                  |                      | .84               | .85                     |
| 6                               |                  |                      | .84               | .84                     |

with a Beckman-Elmer Model DU Infrared recording Infrared spectrophotometer. The samples were held in a salt cell of .025 thickness. The spectra of the two forms are reproduced in Figures 18 and 19.

### Ultraviolet Spectra

The ultraviolet spectra were obtained by means of a Bausch & Lomb "Spectronic" Model 605 recording spectrophotometer.

Spectrometric grade luminous was found satisfactory for precise measurements down to 325 m $\mu$ , since it is transparent in the range in which the material absorbs strongly. The solutions were prepared volumetrically by weighing, under nitrogen, five microliters of the pure compound into a stoppered 100-ml volumetric flask, then filling up to the calibration mark with luminous. The best results were obtained when the flask was about 3/4 full with solvent before introducing the lumene. A ten-microliter syringe was used to measure the volume. Successive dilutions were then made to give solutions of 5, 3, 1 and .5 microliters of volume per 100 ml of solution.

The spectral range of interest in the ultraviolet measurements of the lumene was found to be 300-350 millimicrons. The concentrations of the two lumene

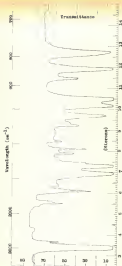


FIGURE 12. Deformed spectrum of KBr-pressed film.



FIGURE 11. Infrared spectrum of 11a—column 3.

were as follows: Inner A,  $2.00 \pm 10^{-4}$  molay/liter; Inner B,  $2.00 \pm 10^{-4}$  molay/liter. Since the concentrations are known, the molar extinction coefficient,  $\epsilon$ , can be calculated from the equation:

$$D = \epsilon c l \quad (7-10)$$

where  $D$  is the optical density, or absorbance, defined by the equation

$$D = \log_{10}(I_0/I) \quad (7-11)$$

$c$  being the concentration in molay/liter and  $l$  the length of the cell. The data are presented in Figure 14 in terms of absorbance against the wavelength.

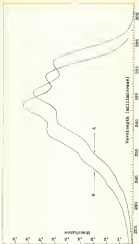


FIGURE 14. Ultraviolet absorption spectra of 3,5-dinitrobenzoic acid A and B in benzene, 10°C.

## CHAPTER VI

### THE THERMAL DECOMPOSITION OF ALL-OLIGOMER

#### Isotermal Interconversion of Isomers

In Chapter III it was established that invariably, at low pyrolysis temperatures, Isomer A was produced, and that at higher temperatures both forms occurred. Upon separating the two isomers by distillation, it was noticed that the refractive index of the distillate gradually increased, as the A form was removed from the mixture. After the refractive index had reached a maximum, it started to decrease. At first this was attributed to some high boiling compounds (such as dimer) reaching the fractionating head. Such compounds are formed during the prolonged heating of the pet mixture. However, a routine chromatographic analysis of the distillate at this point indicated that the amount of Isomer A in the sample was increasing. This curious fact could be explained by assuming that Isomer A was being reformed from B, and perhaps from the depolymerization of the dimer (18, 48). The pet temperature never exceeded 100° C, and it is unlikely that such amount was formed from the polymer at this low temperature, since prolonged heating at 200-300° C is needed to effect very slow dissociation of the dimer.

In view of the facts stated above, it was hypothesized that the pyrolysis of alpha-pinene, at all temperatures, produces Isomer I which then forms Isomer II and that, furthermore, the reaction is reversible. To test this hypothesis, reaction tubes containing only pure I or II were prepared according to the procedure previously outlined. These tubes were heated at different temperatures for varying lengths of time in a thermostated air-bath. Several runs were made, and a typical run starting with pure I is shown in Figure 18. A typical run starting with pure II is also shown in Figure 18. Some clear form in the liquid phase interconversion of alpha-pinene, and a separate analysis was made to determine its presence. The ether boils in the range of 173-175° C at 8 mm Hg and a special high temperature silicone oil chromatographic column was prepared and used.

The next stage in this work was to study kinetically the reversible isomerization of the isomers, and to determine the rate constants and activation energies. For various reasons, it was not possible to carry out the reaction in the vapor phase. The vapor phase interconversion does not produce any dimers or have complicating side reactions, so that the process would probably be a simple reversible first order one.

Approximate Retention Times. Alpha-Phase: 2.8 minutes,  
 Beta-Phase: 4.8 minutes. Alpha-Phase B: 10.8 minutes.  
 Gamma: 4-6 minutes.

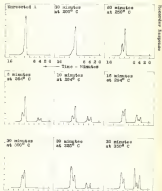


FIGURE 18. Chromatograms showing the influence of temperature on the liquid-phase isomerization of Alpha-Phase A.

Approximate Retention Times, All-trans: 1: 9.8 minutes,  
 All-trans: 2: 19.2 minutes. Pyrenene: 4-5 minutes.

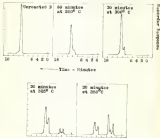


FIGURE 16. Chromatograms Showing the Influence of Temperature on the Liquid-Phase Intercalation of All-trans: 2.

### Sealed Reaction Tubes and Bath

The same procedure as that detailed in Chapter III was used to prepare and fill the sealed reaction tubes. A special silicone oil bath was constructed for the kinetic runs. It consisted of a pyrex jar holding about 4 liters of silicone oil, and it was insulated with asbestos and vermiculite. The cylindrical container was covered with a perforated aluminum plate, to admit the reaction tubes, stirrer, thermometer and heater.

The operating temperatures ranged from 100-300° C, and were difficultly achieved in finding a thermostat that would operate satisfactorily at these temperatures. The Pyrex "Vacuumat", -25 to 300° C, purchased from the Precision Thermometer & Equipment Co., Philadelphia, proved suitable for this work. The bulb of the thermometer was immersed in the silicone oil bath to a depth sufficient to prevent the mercury from distilling up to the top and then down the capillary tube maintaining the contact wire, thus changing the temperature reading. Temperature control was maintained to  $\pm .1$  for any length of time. To prevent heat conduction from the bath to the water through the stainless steel stirrer, a rigid bakelite coupling was used to connect stirrer to motor. The thermometers used were calibrated by the U. S.

Bureau of Standards, and fluctuations were noted with a Beckman differential thermometer with a scale in hundredths of a degree. A 450-watt heater, and a 600-Quartz 450-watt heater were used to bring the bath fluid up to the desired temperature. At that point the 450-watt heater was disconnected and the quartz heater, attached to a sensitive relay through a Varian, was used to keep the temperature at the desired position.

The General Electric EF-80(X) Silicon Field was used for the bath. At the highest temperature of the kinetic runs,  $810^{\circ}\text{C}$ , the fluid "boiled" and during the average length of a run, say, twelve hours, enough oil evaporated to lower the level appreciably. However, it was not necessary to add new oil in the course of a particular run.

#### The Qualitative Determination of Alkylalanes-Fluor Ethoxy-

All quantitative work was done with a Porcin-Flour vapor phase chromatography apparatus. In gas phase chromatography, the area under each peak represents a direct measure of mole percent concentration, since thermal conductivity is linear with number of molecules present. This is true if we assume a constant signal in the detector for each component, and if helium is used as a carrier gas.

An attempt was made to calibrate the column by measuring ratios of peaks of varying concentrations of the isomers, because the peak height is very sensitive to changes of temperature. The temperature regulation in the oven was not adequate either to maintain or reproduce temperature settings. The area under each peak is directly proportional to the concentration of each component, and hence this area relationship was used for calculating mole fractions of each component. Peak areas can be calculated by integration, and there are many ways of doing this. The vapor fractionator did not include an automatic integrator, and the planimeter method was used to evaluate areas. The planimeter was a modified & Rorer Model 4243, with adjustable pole and lever arm.

The advantage of using areas is that results are independent of instrument parameters. The quantitative analysis can be made directly on each recording without the necessity of knowing instrument settings, calibration constants or plots. This cannot be achieved with other methods of analysis.

The column was calibrated by making up, by weight, known mixtures of the two isomers. A constant volume, one microliter, was injected in the instrument with a Hamilton ten-microliter syringe with the Chaney adaptation (Hamilton

Co., Whittier, California). The best method of area assignment is shown in Figure 17 from data of a typical run. Table 8 shows the close agreement of the chromatographic analyses with the absolute method of weighing. To ensure that the agreement was not accidental, several calibrations were made using the same method of area assignment. The results were consistent.

The volume of one microliter was adopted for all runs because, for this amount, areas were in scale at full sensitivity even when a single pure component was used (producing the maximum height).

The problem of the determination of total diene concentration in the mixtures required special consideration. It was not practicable to make separate chromatographic analyses for the diene formed. Fortunately, it was observed that when a constant volume of allyl-oxime-diene mixture was analyzed, the diene concentration could be determined simply by subtracting the area of the reacted mixture from the area of pure isomers. Since the diene had such a high boiling point, they were retained in the reposition block, so that only the isomers in the mixture actually went through the column and were recorded in the chromatogram. The total diene concentrations determined by this method checked very closely with the values reported



FIGURE 17. Typical Chromatograms of ally-estimates 1 and ally-estimates 2 structures.

## References

[illegible]

by Pagliaro at the temperatures (26) for all points. Pagliaro calculated the total diene concentration from weights of the diene separated from the mixture by distillation.

### Procedure for Kinetic Runs

A preliminary run was made at each temperature to determine the approximate period of heating. Kinetic runs were studied at four temperatures: 100.0, 100, 104.0 and 110.0° C. At each temperature a minimum of two independent runs was made, and the starting material for each run consisted of tubes with pure A, pure B, and two mixtures of A and B; one mixture with about 3:1 of A:B, and another with about 3:1 of B:A. Thus four tubes were necessary for each time interval for each independent run. Reaction tubes were filled with a constant amount of about 1/16th ml of the pure isomer, and sealed as previously described; to avoid confusion, each tube was tagged. All the tubes for a particular run were immersed simultaneously in the bath, and there was no provision of heating lag, as the tubes were small and thin-walled. Time was measured with a Stanford Electric Timer (Springfield, Conn.) showing elapsed seconds, and a stopwatch. At the end of a certain time interval tubes were withdrawn from the bath and immediately sprayed with acetone. This treatment

quenched the tubes almost instantaneously, and eliminated the silicone oil on the outside of the tubes. A reacted tube was immediately placed in a freezer, and eventually cracked open under nitrogen and analyzed. Without exception, two analyses were made for each tube. All samples injected were exactly one microliter in volume. Reproducibility was obtained by adopting a standard injection technique. All areas of the chromatograms were determined with a planimeter, and at least six readings of an area were taken and averaged. For each run, one tube was taken through all the filling and sealing operations and served as a control; its measured contents were analyzed and the area equivalent to one microliter of this tube was used as the standard area for that particular run.

#### Methods of Isolating Data

The data from the chromatographic analyses consisted of areas computed from the chromatograms. The area corresponding to each individual isomer was calculated by subtracting the area of the isomer present in a major amount from the total area. The way of assigning areas has already been discussed in the section on the calibration of columns. The total area of the two isomers was then subtracted from the standard area for each run, and this gave the area for total polymer concentration. Since,

as already stated, the area under each peak represents a direct measure of mole percent concentration, the ratio of individual areas to the standard area gives directly the concentration of each component in mole fraction units. A very accurate manual determination of areas with a planimeter requires repeated measurements. At least six tracings were made and averaged to increase the accuracy of the results. Thus over 1800 tracings were necessary for all kinetic runs, including the preliminary work. A typical determination of mole fractions is given below for runs B-IV, in which pure B was reacted for one hour at 20-4.5° C. The standard area for these runs was 2.504 recorder units; the total area of (A + B) dimers was 1.378 wa; the area of A dimer was 1.568 wa, so that by subtraction the area of B was .81 wa, and that for total dimers .648 wa. The mole fractions for A, B and total dimers were therefore .648, .877 and .877 respectively. The recorder units were not converted to square centimeters or square inches by the appropriate planimeter factor, because any such factor would cancel out in the mole fraction calculation.

Another method of tracing the chromatogram areas was used and it consisted of cutting and weighing the tracings. Here it was assumed that the recording paper

use of uniform composition. This procedure was used in some of the preliminary and calibration runs and, although the results were comparable to the plasterboard method, it was excessively time-consuming and hence impractical.

At 100.0° C three independent runs were made, instead of the usual two at other temperatures. The reason for this was to check the reproducibility of the data. The precision was good, and since there was no way of telling which run was more accurate than any other, the two (or three for the first run) were averaged and this result was used in the calculations.

The average results of the analyses for the following runs are given in Tables 6-8a.

|              |          |          |            |             |
|--------------|----------|----------|------------|-------------|
| A-T-ah, 6-PI | B-11-ah  | AB-11-ah | AB-PI1-ah  | at 100.0° C |
| A-PI1-ah     | B-PI1-ah | AB-IV-ah | AB-PI1-ah  | at 100° C   |
| A-PI11-ah    | B-11-ah  | AB-T-ah  | AB-PI11-ah | at 104.0° C |
| A-11-ah      | B-T-ah   | AB-T1-ah | AB-11-ah   | at 105° C   |

The designations for the runs are: the first capital letter(s), such as A for example, means that pure A was used as the starting material; B means that pure B was the starting material; AB means that a mixture of A and B was used, etc. The Roman numeral designates the run, and the small letters, two identical independent runs.

Plots of mole fractions against time, from the data in tables 4-24 were made and are given in Figures 18-24. Curves were drawn through the points, then these normalized curves were used in the calculations.

### Calculations

From the normalized curves, 24 tables of two variables were compiled: concentration in mole fractions units, versus time in minutes. In order to obtain the derivative or rate  $-dy/dt$ , where  $y$  is A or B, an optical device was tried at first and then graphical differentiation was used. Both methods proved tedious, time-consuming and inaccurate. For example, the optical device, consisting of a right prism and a half-silvered mirror, could not be used to obtain initial rates, and in the mathematical method there was considerable uncertainty in drawing a smooth curve through the points  $\Delta y/\Delta t$  to obtain the rate as a function of time.

It was therefore decided to derive equations that would fit the experimental curves, and then simply obtain the derivatives at any desired points. An IBM 480 computer was used in connection with this method. The data from the 24 tables were used as the input for an 18-1 programming. Concentration,  $y$ , was regarded as the dependent variable

and first, second, third and fourth degree equations were set up as follows:

$$P = a + b t \quad \text{VI-1}$$

$$P = a_1 + b_1 t + c_1 t^2 \quad \text{VI-2}$$

$$P = a_2 + b_2 t + c_2 t^2 + d_2 t^3 \quad \text{VI-3}$$

$$P = a_3 + b_3 t + c_3 t^2 + d_3 t^3 + e_3 t^4 \quad \text{VI-4}$$

The output from the IBM-1 programming comprised values of the constants of equations VI-1 to VI-4, as well as other statistical criteria. The data from this operation were used to obtain the derivatives and their logarithms. The values of the reaction velocities for all runs are given in Tables 25-28. The tables also include the time and concentration variations.

TABLE 2

KINETIC DATA FROM RUNS A-T-48, A-T-49 AT 100.0° C

| Reaction<br>Time in Hours | Concentrations in Mole Fraction Units |          |               |
|---------------------------|---------------------------------------|----------|---------------|
|                           | Isomer A                              | Isomer B | Total Polymer |
| 0                         | .00                                   | .00      | 0.            |
| .25                       | .026                                  | .126     | .152          |
| .75                       | .028                                  | .087     | .115          |
| 1                         | .028                                  | .100     | .128          |
| 2                         | .03                                   | .128     | .158          |
| 3                         | .029                                  | .130     | .159          |
| 4                         | .029                                  | .128     | .157          |
| 5                         | .029                                  | .125     | .154          |
| 6                         | .028                                  | .125     | .153          |
| 7                         | .028                                  | .124     | .152          |
| 8                         | .028                                  | .124     | .152          |
| 10                        | .024                                  | .107     | .131          |
| 12                        | .024                                  | .112     | .136          |
| 14                        | .024                                  | .108     | .132          |
| 16                        | .023                                  | .103     | .126          |
| 18                        | .021                                  | .100     | .121          |
| 19.5                      | .027                                  | .100     | .127          |

TABLE 14  
KINETIC DATA FROM PLOTS A-VII AT 500° C

| Reaction<br>Time in Hours | Saponification in Mole Fraction Units |         |             |
|---------------------------|---------------------------------------|---------|-------------|
|                           | Inner A                               | Inner B | Dist. Rings |
| 0                         | .07                                   | .03     | 0.          |
| 1                         | .034                                  | .101    | .083        |
| 2                         | .091                                  | .128    | .451        |
| 3                         | .030                                  | .134    | .507        |
| 4                         | .028                                  | .128    | .838        |
| 5                         | .100                                  | .134    | .879        |
| 6                         | .100                                  | .130    | .708        |
| 7                         | .104                                  | .113    | .748        |
| 8                         | .100                                  | .121    | .754        |
| 10                        | .089                                  | .121    | .778        |
| 11                        | .083                                  | .121    | .798        |
| 12                        | .074                                  | .117    | .802        |

TABLE 11  
KINETIC DATA FROM RUNS A-VIII AT 304.5° C

| Reaction<br>Time in Hours | Concentration in Gals. Fraction Solids |         |              |
|---------------------------|----------------------------------------|---------|--------------|
|                           | Layer A                                | Layer B | Total Solids |
| 0                         | .000                                   | .000    | 0            |
| .2                        | .774                                   | .071    | .845         |
| 1                         | .048                                   | .193    | .241         |
| 1.5                       | .048                                   | .100    | .148         |
| 2                         | .000                                   | .100    | .100         |
| 3                         | .000                                   | .100    | .100         |
| 4                         | .000                                   | .100    | .100         |
| 5                         | .000                                   | .100    | .100         |
| 6                         | .000                                   | .100    | .100         |
| 7                         | .000                                   | .100    | .100         |
| 8                         | .000                                   | .100    | .100         |
| 10                        | .000                                   | .100    | .100         |

TABLE 13  
KINETIC DATA FROM RUNS 4-IX AT 510° C

| Reaction<br>Time in Hours | Decomposition in High Pressure Cells |          |               |
|---------------------------|--------------------------------------|----------|---------------|
|                           | Runner A                             | Runner B | Total Release |
| 0                         | .070                                 | .400     | 0.            |
| .30                       | .010                                 | .004     | .117          |
| .60                       | .071                                 | .160     | .230          |
| .75                       | .000                                 | .137     | .238          |
| 1                         | .000                                 | .137     | .240          |
| 2.0                       | .070                                 | .141     | .211          |
| 3                         | .010                                 | .147     | .207          |
| 2.0                       | .060                                 | .130     | .190          |
| 3                         | .000                                 | .030     | .040          |
| 6                         | .171                                 | .100     | .270          |
| 6                         | .100                                 | .00      | .100          |

TABLE 13  
KINETIC DATA FROM RUNS 3-11 AT 189.4° C

| Reaction<br>Time in Hours | Concentrations in Mole Fraction Units |          |              |
|---------------------------|---------------------------------------|----------|--------------|
|                           | Isomer A                              | Isomer B | Total Kinere |
| 0                         | .000                                  | .000     | 0            |
| 1                         | .040                                  | .013     | .143         |
| 2                         | .042                                  | .014     | .166         |
| 3                         | .050                                  | .020     | .176         |
| 4                         | .050                                  | .019     | .169         |
| 5                         | .048                                  | .019     | .170         |
| 6                         | .050                                  | .020     | .177         |
| 7                         | .050                                  | .020     | .162         |
| 8                         | .050                                  | .020     | .162         |
| 10                        | .045                                  | .020     | .165         |
| 11                        | .045                                  | .020     | .165         |
| 12.5                      | .045                                  | .024     | .174         |
| 14                        | .042                                  | .026     | .172         |
| 15                        | .034                                  | .024     | .168         |
| 17.5                      | .028                                  | .019     | .158         |

TABLE 14

KINETIC DATA FROM PAGES 2-111 AT 300° C

| Reaction<br>Time in Hours | Concentration in Total Fraction Factor |          |               |
|---------------------------|----------------------------------------|----------|---------------|
|                           | Factor A                               | Factor B | Total Kinetic |
| 0                         | .000                                   | .000     | 0             |
| 1                         | .000                                   | .000     | .000          |
| 2                         | .000                                   | .000     | .000          |
| 3                         | .000                                   | .000     | .000          |
| 4                         | .000                                   | .000     | .000          |
| 5                         | .000                                   | .000     | .000          |
| 6                         | .000                                   | .000     | .000          |
| 7                         | .000                                   | .000     | .000          |
| 8                         | .000                                   | .000     | .000          |
| 10                        | .000                                   | .000     | .000          |
| 12                        | .000                                   | .000     | .000          |

TABLE 10  
KINETIC DATA FROM PAPER 2-17 AT 204.5° C

| Fraction<br>Time in hours | Concentrations in Each Fraction, Mole/l. |            |               |
|---------------------------|------------------------------------------|------------|---------------|
|                           | Fraction A                               | Fraction B | Total Kinetic |
| 0                         | .000                                     | .000       | 0.            |
| .5                        | .048                                     | .019       | .134          |
| 1                         | .048                                     | .015       | .177          |
| 1.5                       | .052                                     | .009       | .248          |
| 2                         | .052                                     | .005       | .408          |
| 3                         | .050                                     | .012       | .633          |
| 4                         | .041                                     | .020       | .802          |
| 5                         | .041                                     | .022       | .823          |
| 6                         | .041                                     | .017       | .808          |
| 7                         | .038                                     | .024       | .793          |
| 8                         | .041                                     | .021       | .714          |
| 10                        | .034                                     | .019       | .788          |

TABLE 10  
KINETIC DATA FROM RUNS 3-7 AT 310° C

| Reaction<br>Time in hours | Concentrations in Mole Fraction Units |          |                 |
|---------------------------|---------------------------------------|----------|-----------------|
|                           | Isomer A                              | Isomer B | Trigl. Elements |
| 0                         | .000                                  | .070     | 0               |
| .20                       | .048                                  | .030     | .100            |
| .5                        | .080                                  | .070     | .200            |
| .75                       | .090                                  | .070     | .070            |
| 1                         | .090                                  | .060     | .200            |
| 1.5                       | .090                                  | .060     | .400            |
| 2                         | .091                                  | .059     | .500            |
| 2.5                       | .091                                  | .059     | .500            |
| 3                         | .090                                  | .060     | .500            |
| 4                         | .090                                  | .060     | .500            |
| 5                         | .090                                  | .060     | .500            |

TABLE 17  
KINETIC DATA FROM RUNS 22-27 AT 180.0° C

| Reaction<br>Time in Hours | Concentration in Hole Fraction Units |        |             |
|---------------------------|--------------------------------------|--------|-------------|
|                           | Run 24                               | Run 25 | Total Holes |
| 0                         | .000                                 | .000   | 0           |
| 1                         | .012                                 | .007   | .180        |
| 2                         | .020                                 | .009   | .200        |
| 3                         | .030                                 | .010   | .240        |
| 4                         | .040                                 | .010   | .260        |
| 5                         | .050                                 | .010   | .260        |
| 6                         | .073                                 | .010   | .280        |
| 7                         | .100                                 | .010   | .300        |
| 8                         | .140                                 | .010   | .340        |
| 10                        | .114                                 | .010   | .210        |
| 11                        | .100                                 | .010   | .200        |
| 12.5                      | .080                                 | .010   | .190        |
| 14                        | .060                                 | .010   | .160        |
| 16                        | .050                                 | .010   | .150        |
| 17.5                      | .001                                 | .007   | .008        |

TABLE 10

KINETIC DATA FROM RUNS 48-57 AT 250° C

| Reaction<br>Time in hours | Concentrations in Mole Fractions Units |          |             |
|---------------------------|----------------------------------------|----------|-------------|
|                           | Linear A                               | Linear B | Total Moles |
| 0                         | .715                                   | .275     | 0           |
| 1                         | .488                                   | .508     | .994        |
| 2                         | .366                                   | .631     | .997        |
| 3                         | .308                                   | .687     | .995        |
| 4                         | .269                                   | .729     | .994        |
| 5                         | .238                                   | .762     | .999        |
| 6                         | .205                                   | .795     | .999        |
| 7                         | .178                                   | .822     | .999        |
| 8                         | .152                                   | .848     | .999        |
| 11                        | .095                                   | .905     | .999        |
| 14                        | .066                                   | .934     | .999        |
| 18                        | .045                                   | .955     | .999        |

TABLE 20  
KINETIC DATA FROM RUNS 42-7 AT 204.5° C

| Reaction<br>Time in hours | Concentration in Mole Fraction Units |          |             |
|---------------------------|--------------------------------------|----------|-------------|
|                           | Isomer A                             | Isomer B | Total Moles |
| 0                         | .718                                 | .276     | 0           |
| .5                        | .681                                 | .317     | .302        |
| 1                         | .65                                  | .355     | .333        |
| 1.5                       | .621                                 | .374     | .414        |
| 2                         | .584                                 | .416     | .510        |
| 3                         | .558                                 | .471     | .607        |
| 5                         | .497                                 | .503     | .807        |
| 6                         | .488                                 | .512     | .719        |
| 7                         | .483                                 | .517     | .723        |
| 8                         | .484                                 | .513     | .708        |
| 10                        | .486                                 | .512     | .708        |

TABLE 30  
KINETIC DATA FROM PAGES 48-71 AT 510° C

| Reaction<br>Time in Hours | Concentrations in Gals Fraction Units |          |              |
|---------------------------|---------------------------------------|----------|--------------|
|                           | Isomer A                              | Isomer B | Total Alkane |
| 0                         | .718                                  | .274     | 0            |
| .50                       | .600                                  | .280     | .008         |
| .5                        | .520                                  | .300     | .001         |
| .70                       | .494                                  | .320     | .001         |
| 1                         | .414                                  | .316     | .008         |
| 1.5                       | .360                                  | .302     | .009         |
| 2                         | .323                                  | .350     | .004         |
| 2.5                       | .300                                  | .300     | .004         |
| 3                         | .183                                  | .179     | .002         |
| 4                         | .148                                  | .160     | .004         |
| 6                         | .138                                  | .140     | .002         |

TABLE XI

KINETIC DATA FROM RUNS AD-171 AT 100.0° C

| Reaction<br>Time in Hours | Concentration in Mole Fraction Units |          |               |
|---------------------------|--------------------------------------|----------|---------------|
|                           | Isomer A                             | Isomer B | Total Olefins |
| 0                         | .000                                 | .000     | 0.            |
| 1                         | .263                                 | .407     | .670          |
| 2                         | .282                                 | .420     | .702          |
| 3                         | .296                                 | .440     | .736          |
| 4                         | .304                                 | .454     | .758          |
| 5                         | .306                                 | .466     | .772          |
| 6                         | .312                                 | .466     | .778          |
| 7                         | .316                                 | .467     | .783          |
| 8                         | .317                                 | .470     | .787          |
| 10                        | .322                                 | .470     | .792          |
| 11                        | .325                                 | .477     | .802          |
| 12.5                      | .328                                 | .477     | .805          |
| 14                        | .331                                 | .477     | .808          |
| 15.5                      | .337                                 | .480     | .817          |

TABLE 22

KINETIC DATA FROM THERM GR-TII AT 200° C

| Reaction<br>Time in Hours | Concentration in mole Fraction Toluene |          |            |
|---------------------------|----------------------------------------|----------|------------|
|                           | Isomer A                               | Isomer B | Total Mole |
| 0                         | .000                                   | .000     | 0.         |
| 1                         | .000                                   | .000     | .000       |
| 2                         | .000                                   | .000     | .000       |
| 3                         | .000                                   | .000     | .000       |
| 4                         | .000                                   | .000     | .000       |
| 5                         | .001                                   | .000     | .010       |
| 6                         | .004                                   | .000     | .040       |
| 7                         | .004                                   | .000     | .040       |
| 8                         | .008                                   | .000     | .080       |
| 10                        | .008                                   | .004     | .052       |
| 12                        | .008                                   | .003     | .040       |
| 15                        | .008                                   | .001     | .030       |

TABLE 20

KINETIC DATA FROM RUNS 21-7121 AT 204.0° C

| Reaction<br>Time in Hours | Concentration in Mole Fraction Units |         |             |
|---------------------------|--------------------------------------|---------|-------------|
|                           | Inner A                              | Inner B | Total Moles |
| 0                         | .000                                 | .000    | 0.          |
| .5                        | .004                                 | .002    | .006        |
| 1                         | .008                                 | .007    | .015        |
| 1.5                       | .010                                 | .008    | .018        |
| 2                         | .012                                 | .009    | .021        |
| 3                         | .015                                 | .010    | .025        |
| 4                         | .018                                 | .011    | .029        |
| 5                         | .020                                 | .012    | .032        |
| 6                         | .022                                 | .013    | .035        |
| 7                         | .024                                 | .014    | .038        |
| 8                         | .026                                 | .015    | .041        |
| 10                        | .030                                 | .018    | .048        |

TABLE 14  
KINETIC DATA FROM RUNS 24-32 AT 210° C

| Reaction<br>Time in Hours | Concentrations in Mole Fraction Units |          |              |
|---------------------------|---------------------------------------|----------|--------------|
|                           | Isomer A                              | Isomer B | Total Kinase |
| 0                         | .847                                  | .743     | 0.           |
| .05                       | .818                                  | .725     | .008         |
| .10                       | .797                                  | .707     | .016         |
| .15                       | .783                                  | .689     | .024         |
| .2                        | .767                                  | .673     | .031         |
| .2.5                      | .746                                  | .653     | .047         |
| .3                        | .737                                  | .645     | .053         |
| .3.5                      | .729                                  | .633     | .058         |
| .4                        | .721                                  | .623     | .064         |
| .5                        | .704                                  | .607     | .074         |
| .6                        | .695                                  | .599     | .078         |



FIGURE 14. Double Ratio from Data 1-7 and 8-11 at 100.5° C.

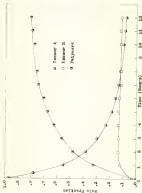


FIGURE 10. Evolution of Data Fraction from Time 0 to 12 hours.

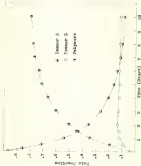


FIGURE 10. Kinetics Data from Run A-111 at 404.7° C.

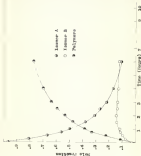


FIGURE 10. Kinetic Data from 0-24 at 100°C.

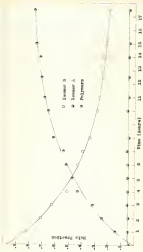


FIGURE 10. Kinetics of the reaction of monomer A with monomer B at 100°C.



FIGURE 12. Change Rate from Run 3-110 at 300° C.



FIGURE 14. Mole fraction of monomer and polymer vs. time at 20°C, 30°C, and 40°C.



Figure 10. Kinetic data from runs B-X at 200°C.



FIGURE 33. Kinetic Data from Runs 40-41 at 100, 150°C.



FIGURE 10. Effect of time on the concentration of monomer A, monomer B, and polymer.



FIGURE 10. Kinetic data from Run 23-7 at 20-25°C.

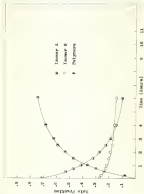


FIGURE 10. Kinetic Data from Runs 10-12 at 100°C.



FIGURE 20. Kinetics of the reaction of monomer A with monomer B at 100°C.

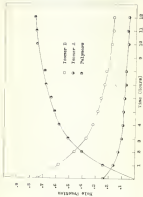


FIGURE 11. Kinetic Data from Run 10-101 at 200°C.

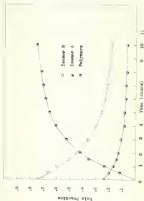


FIGURE 23. Kinetic data from Run 21-4711 at 304.5° C.



FIGURE 10. Kinetic Data from Run 10-11 at 110°C.

TABLE III  
 FTS, DISPERSSION AND RARE DATA AT 100, 200, 300, 400, 500, 600, 700, AND 800

| Time<br>in<br>minutes<br>$t_{\text{exp}}$ | Rate<br>Function<br>Factor A<br>$k_p \times 10^3$ | $\frac{1-\theta(t_{\text{exp}})}{t_{\text{exp}}}$ |       | Rate<br>Function<br>Factor B<br>$k_d \times 10^3$ | $-\log_{10}(\theta) \times 10^2$ |       |
|-------------------------------------------|---------------------------------------------------|---------------------------------------------------|-------|---------------------------------------------------|----------------------------------|-------|
|                                           |                                                   | FT-3                                              | FT-5  |                                                   | FT-3                             | FT-5  |
| 0                                         | —                                                 | 0.000                                             | 0.000 | —                                                 | 0.000                            | 0.000 |
| 20                                        | 0.07                                              | 0.150                                             | 0.150 | 0.07                                              | 1.020                            | 0.990 |
| 40                                        | 0.07                                              | 0.175                                             | 0.175 | 0.07                                              | 1.200                            | 1.050 |
| 60                                        | 0.07                                              | 0.200                                             | 0.200 | 0.07                                              | 1.310                            | 1.080 |
| 80                                        | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.400                            | 1.090 |
| 100                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.470                            | 1.090 |
| 120                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.530                            | 1.090 |
| 140                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.580                            | 1.090 |
| 160                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.620                            | 1.090 |
| 180                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.650                            | 1.090 |
| 200                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.680                            | 1.090 |
| 220                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.700                            | 1.090 |
| 240                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.720                            | 1.090 |
| 260                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.740                            | 1.090 |
| 280                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.760                            | 1.090 |
| 300                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.780                            | 1.090 |
| 320                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.800                            | 1.090 |
| 340                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.820                            | 1.090 |
| 360                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.840                            | 1.090 |
| 380                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.860                            | 1.090 |
| 400                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.880                            | 1.090 |
| 420                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.900                            | 1.090 |
| 440                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.920                            | 1.090 |
| 460                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.940                            | 1.090 |
| 480                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.960                            | 1.090 |
| 500                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 1.980                            | 1.090 |
| 520                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 2.000                            | 1.090 |
| 540                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 2.020                            | 1.090 |
| 560                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 2.040                            | 1.090 |
| 580                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 2.060                            | 1.090 |
| 600                                       | 0.07                                              | 0.000                                             | 0.000 | 0.07                                              | 2.080                            | 1.090 |

TABLE 2  
 TSS, CONCENTRATION AND TIME DATA FOR THE 1-FTI AND 2-FTI

| Time<br>to<br>maxima<br>(s) | Peak<br>concentration<br>( $\mu\text{g/l}$ ) | $\frac{1-\Delta\text{C}/\text{C}_0}{\text{C}_0} \times 10^3$ |       | Peak<br>concentration<br>( $\mu\text{g/l}$ ) | $\frac{1-\Delta\text{C}/\text{C}_0}{\text{C}_0} \times 10^3$ |       |
|-----------------------------|----------------------------------------------|--------------------------------------------------------------|-------|----------------------------------------------|--------------------------------------------------------------|-------|
|                             |                                              | 1-FTI                                                        | 2-FTI |                                              | 1-FTI                                                        | 2-FTI |
| 1                           | 1.07                                         | 0.012                                                        | 0.014 | 1.07                                         | 0.013                                                        | 0.013 |
| 20                          | 0.190                                        | —                                                            | —     | 0.19                                         | —                                                            | —     |
| 30                          | 0.093                                        | 0.019                                                        | 0.019 | 0.093                                        | 0.019                                                        | 0.019 |
| 40                          | 0.066                                        | 0.013                                                        | 0.018 | 0.066                                        | 0.017                                                        | 0.019 |
| 50                          | 0.050                                        | 0.010                                                        | 0.017 | 0.050                                        | 0.015                                                        | 0.014 |
| 60                          | 0.043                                        | 0.009                                                        | 0.014 | 0.043                                        | 0.012                                                        | 0.013 |
| 100                         | 0.020                                        | 0.013                                                        | 0.019 | 0.020                                        | 0.016                                                        | 0.016 |
| 150                         | 0.009                                        | 0.010                                                        | 0.019 | 0.009                                        | 0.014                                                        | 0.016 |
| 200                         | 0.040                                        | 0.019                                                        | 0.019 | 0.040                                        | 0.014                                                        | 0.013 |
| 250                         | 0.010                                        | 0.013                                                        | 0.019 | 0.010                                        | 0.010                                                        | 0.014 |
| 300                         | 0.009                                        | 0.010                                                        | 0.014 | 0.009                                        | 0.008                                                        | 0.010 |
| 350                         | 0.010                                        | 0.019                                                        | 0.017 | 0.010                                        | 0.014                                                        | 0.013 |
| 400                         | 0.009                                        | 0.019                                                        | 0.013 | 0.009                                        | 0.010                                                        | 0.010 |

TABLE IV  
 TMS, COMPOSITION AND NAME DATA AT 264.1° C FOR MOPS 4-7011 AND 3-77

| Time<br>in<br>minutes<br>( $t_p - t_0$ ) | Sulfur<br>Fraction<br>$\bar{X}_p \times 10^3$ | $\frac{(-d\bar{X}_p/dt)}{dt} \times 10^3$ |       | Sulfur<br>Fraction<br>$\bar{X}_p \times 10^3$ | $\frac{(-d\bar{X}_p/dt)}{dt} \times 10^3$ |       |
|------------------------------------------|-----------------------------------------------|-------------------------------------------|-------|-----------------------------------------------|-------------------------------------------|-------|
|                                          |                                               | 77-3                                      | 77-3  |                                               | 77-3                                      | 77-3  |
| 0                                        | 0.00                                          | 2.390                                     | 0.073 | 0.00                                          | 2.390                                     | 4.409 |
| 30                                       | 0.03                                          | —                                         | —     | 0.03                                          | —                                         | —     |
| 60                                       | 0.05                                          | 2.008                                     | 4.098 | 0.05                                          | 2.000                                     | 3.030 |
| 90                                       | 0.070                                         | 2.000                                     | 3.000 | 0.06                                          | 2.011                                     | 2.123 |
| 120                                      | 0.080                                         | 1.714                                     | 2.100 | 0.07                                          | 2.001                                     | 2.000 |
| 150                                      | 0.09                                          | 1.518                                     | 2.200 | 0.08                                          | 2.000                                     | 2.040 |
| 180                                      | 0.10                                          | 1.504                                     | 1.800 | 0.09                                          | 2.000                                     | 2.001 |
| 210                                      | 0.11                                          | 1.400                                     | 2.110 | 0.10                                          | 2.004                                     | 2.005 |
| 240                                      | 0.12                                          | 1.300                                     | 2.040 | 0.11                                          | 2.014                                     | 2.010 |
| 270                                      | 0.13                                          | 1.200                                     | 2.000 | 0.12                                          | 2.000                                     | 2.000 |
| 300                                      | 0.14                                          | 1.143                                     | 2.000 | 0.13                                          | 2.000                                     | 2.000 |
| 330                                      | 0.15                                          | 1.000                                     | 1.000 | 0.14                                          | 1.999                                     | 1.999 |
| 360                                      | 0.16                                          | 1.000                                     | 0.000 | 0.15                                          | 1.999                                     | 1.999 |

TABLE III  
TIME, CONCENTRATION AND RATE DATA AT 210° C FOR RIND A-III AND B-V

| Time<br>in<br>minutes<br>$t_p \times 10^3$ | Rate<br>Fraction<br>Increase $A$<br>$A_p \times 10^3$ | $(A_{\infty}/A_p) \times 10^3$ | Rate<br>Fraction<br>Increase $B$<br>$B_p \times 10^3$ | $(B_{\infty}/B_p) \times 10^3$ |
|--------------------------------------------|-------------------------------------------------------|--------------------------------|-------------------------------------------------------|--------------------------------|
| 0                                          |                                                       |                                |                                                       |                                |
| 20                                         | -37                                                   | 4.209                          |                                                       | 4.300                          |
| 40                                         | -46                                                   | "                              |                                                       | "                              |
| 60                                         | -48                                                   | 3.303                          |                                                       | 2.243                          |
| 70                                         | -43                                                   | 3.713                          |                                                       | 3.374                          |
| 85                                         | -36                                                   | 3.608                          |                                                       | 3.003                          |
| 95                                         | -24                                                   | 3.503                          |                                                       | 3.003                          |
| 105                                        | -20                                                   | 3.003                          |                                                       | 3.003                          |
| 120                                        | -20                                                   | 3.003                          |                                                       | 3.003                          |
| 150                                        | -20                                                   | 3.003                          |                                                       | 3.003                          |
| 160                                        | -22                                                   | 3.003                          |                                                       | 3.003                          |
| 240                                        | -13                                                   | 3.003                          |                                                       | 3.003                          |

TABLE 29

EDS, CONCENTRATION AND RATE DATA AT 100.0° C FOR PHS 18-11

| Time<br>in<br>Minutes | Sole<br>Product<br>Number 1 | $\frac{(-dS/dt) \times 10^3}{M-1}$ | Sole<br>Product<br>Number 2 | $\frac{(-dS/dt) \times 10^3}{M-1}$ |
|-----------------------|-----------------------------|------------------------------------|-----------------------------|------------------------------------|
| 0                     |                             |                                    |                             |                                    |
| 20                    | -61                         | 1.111                              | -60                         | 1.000                              |
| 40                    | -64                         | 1.002                              | -63                         | 1.000                              |
| 60                    | -63                         | 1.000                              | -63                         | 1.000                              |
| 80                    | -64                         | 1.002                              | -60                         | 1.000                              |
| 90                    | -63                         | 1.000                              | -63                         | 1.000                              |
| 100                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 120                   | -63                         | 1.000                              | -63                         | 1.000                              |
| 140                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 160                   | -63                         | 1.000                              | -63                         | 1.000                              |
| 180                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 200                   | -63                         | 1.000                              | -63                         | 1.000                              |
| 220                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 240                   | -63                         | 1.000                              | -63                         | 1.000                              |
| 260                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 280                   | -63                         | 1.000                              | -63                         | 1.000                              |
| 300                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 320                   | -63                         | 1.000                              | -63                         | 1.000                              |
| 340                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 360                   | -63                         | 1.000                              | -63                         | 1.000                              |
| 380                   | -64                         | 1.002                              | -60                         | 1.000                              |
| 400                   | -63                         | 1.000                              | -63                         | 1.000                              |

TABLE 20

Time, concentration and rate data at 300° C per 40-70 mm.

| Time<br>in<br>minutes | Rate<br>fraction<br>factor, $k$ | $\frac{d(\text{MnO})}{dt} \times 10^3$<br>M-2 | Rate<br>fraction<br>factor, $k$ | $\frac{d(\text{MnO})}{dt} \times 10^3$<br>M-2 | $\frac{d(\text{MnO})}{dt} \times 10^3$<br>M-2 |
|-----------------------|---------------------------------|-----------------------------------------------|---------------------------------|-----------------------------------------------|-----------------------------------------------|
| 0                     | 0.00                            | 0.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 20                    | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 40                    | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 60                    | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 70                    | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 80                    | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 90                    | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 100                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 120                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 140                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 160                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 180                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 200                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 220                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 240                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 260                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 280                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |
| 300                   | 0.00                            | 1.000                                         | 0.00                            | 0.000                                         | 0.00                                          |

TABLE XI

HPLC, CONCENTRATIONS AND RATE DATA AT 60°C.<sup>a</sup> 6 RUN 42-17 1100

| Time<br>in<br>minutes | Sol-gel<br>Fraction<br>Number A | $\frac{d-50/\text{mol}}{M-0}$ |        | $\frac{d-50/\text{mol}}{M-0} \times 10^3$ |        | Sol-gel<br>Fraction<br>Number B |        | $\frac{d-50/\text{mol}}{M-0} \times 10^3$ |        |
|-----------------------|---------------------------------|-------------------------------|--------|-------------------------------------------|--------|---------------------------------|--------|-------------------------------------------|--------|
|                       |                                 | $M-0$                         | $d-50$ | $M-0$                                     | $d-50$ | $M-0$                           | $d-50$ | $M-0$                                     | $d-50$ |
| 0                     |                                 |                               |        |                                           |        |                                 |        |                                           |        |
| 5                     | 015                             | 1.000                         | 0.000  | 0.000                                     | 0.000  | 000                             | 000    | 000                                       | 000    |
| 10                    | 020                             | 0.997                         | 0.003  | 0.003                                     | 0.003  | 001                             | 001    | 001                                       | 001    |
| 45                    | 00                              | 0.993                         | 0.007  | 0.007                                     | 0.007  | 004                             | 004    | 004                                       | 004    |
| 60                    | 00                              | 0.986                         | 0.014  | 0.014                                     | 0.014  | 009                             | 009    | 009                                       | 009    |
| 75                    | 0018                            | 0.980                         | 0.020  | 0.020                                     | 0.020  | 011                             | 011    | 011                                       | 011    |
| 90                    | 0030                            | 0.973                         | 0.027  | 0.027                                     | 0.027  | 016                             | 016    | 016                                       | 016    |
| 105                   | 0042                            | 0.965                         | 0.035  | 0.035                                     | 0.035  | 021                             | 021    | 021                                       | 021    |
| 120                   | 0053                            | 0.956                         | 0.044  | 0.044                                     | 0.044  | 026                             | 026    | 026                                       | 026    |
| 135                   | 0065                            | 0.946                         | 0.054  | 0.054                                     | 0.054  | 031                             | 031    | 031                                       | 031    |
| 150                   | 0077                            | 0.935                         | 0.065  | 0.065                                     | 0.065  | 037                             | 037    | 037                                       | 037    |
| 165                   | 0089                            | 0.923                         | 0.077  | 0.077                                     | 0.077  | 043                             | 043    | 043                                       | 043    |
| 180                   | 0100                            | 0.910                         | 0.089  | 0.089                                     | 0.089  | 049                             | 049    | 049                                       | 049    |
| 195                   | 0110                            | 0.896                         | 0.100  | 0.100                                     | 0.100  | 055                             | 055    | 055                                       | 055    |
| 210                   | 0120                            | 0.881                         | 0.112  | 0.112                                     | 0.112  | 061                             | 061    | 061                                       | 061    |
| 225                   | 0130                            | 0.865                         | 0.125  | 0.125                                     | 0.125  | 067                             | 067    | 067                                       | 067    |
| 240                   | 0140                            | 0.848                         | 0.140  | 0.140                                     | 0.140  | 073                             | 073    | 073                                       | 073    |
| 255                   | 0150                            | 0.830                         | 0.150  | 0.150                                     | 0.150  | 079                             | 079    | 079                                       | 079    |

TABLE III  
TIME, CONCENTRATION RATE DATA AT 210°C FOR AB-VI BLENDS

| Time<br>in<br>minutes | Intr.<br>Pressure<br>mm-Hg | $\frac{d-AB/dt}{dt}$ , g./g. <sup>2</sup> |       | Intr.<br>Pressure<br>mm-Hg | $\frac{d-AB/dt}{dt}$ , g./g. <sup>2</sup> |       |
|-----------------------|----------------------------|-------------------------------------------|-------|----------------------------|-------------------------------------------|-------|
|                       |                            | VI-2                                      | VI-3  |                            | VI-2                                      | VI-3  |
| 0                     | -97.8                      | 2.799                                     | 5.455 | -97.3                      | .721                                      | 1.129 |
| 20                    | -95.6                      | 2.594                                     | 4.128 | -95.6                      | .704                                      | .846  |
| 40                    | -93.6                      | 2.126                                     | 3.750 | -93.6                      | .687                                      | .728  |
| 60                    | -91.5                      | 2.095                                     | 3.282 | -91.5                      | .645                                      | .678  |
| 80                    | -89.4                      | 2.825                                     | 2.535 | -89.5                      | .654                                      | .598  |
| 100                   | -94.5                      | 2.654                                     | 2.709 | -90.0                      | .653                                      | .528  |
| 120                   | -92.5                      | 2.487                                     | 2.824 | -90.5                      | .645                                      | .482  |
| 140                   | -90.0                      | 2.233                                     | 2.155 | -90.1                      | .491                                      | .465  |
| 160                   | -88.0                      | 2.173                                     | 1.827 | -89.5                      | .495                                      | .445  |
| 180                   | -86.0                      | 1.801                                     | .882  | -89.3                      | .493                                      | .443  |
| 200                   | -84.0                      | 1.54                                      | .672  | -89.2                      | .487                                      | .436  |

TABLE 85  
TDS, DISPERSED AND APP. DATA AT 800° C FOR 30-70 Ti-30

| Time<br>in<br>minutes | TDS<br>Percent<br>Driver 1 | $\Delta_{\text{app}}/\Delta t$ , g. $\text{kg}^{-1}$ |       | TDS<br>Percent<br>Driver 2 | $\Delta_{\text{app}}/\Delta t$ , g. $\text{kg}^{-1}$ |        |
|-----------------------|----------------------------|------------------------------------------------------|-------|----------------------------|------------------------------------------------------|--------|
|                       |                            | 77-3                                                 | 77-3  |                            | 77-3                                                 | 77-3   |
| 0                     | -0.0                       | 0.00                                                 | 0.000 | 0.0                        | 0.00                                                 | 0.000  |
| 20                    | -1.00                      | -0.00                                                | -0.00 | 0.0                        | 0.00                                                 | 0.000  |
| 40                    | -1.75                      | -0.01                                                | -0.01 | -0.0                       | -0.01                                                | -0.000 |
| 60                    | -2.40                      | -0.02                                                | -0.02 | -0.0                       | -0.02                                                | -0.000 |
| 80                    | -3.00                      | -0.03                                                | -0.03 | -0.0                       | -0.03                                                | -0.000 |
| 100                   | -3.60                      | -0.04                                                | -0.04 | -0.0                       | -0.04                                                | -0.000 |
| 120                   | -4.20                      | -0.05                                                | -0.05 | -0.0                       | -0.05                                                | -0.000 |
| 140                   | -4.80                      | -0.06                                                | -0.06 | -0.0                       | -0.06                                                | -0.000 |
| 160                   | -5.40                      | -0.07                                                | -0.07 | -0.0                       | -0.07                                                | -0.000 |
| 180                   | -6.00                      | -0.08                                                | -0.08 | -0.0                       | -0.08                                                | -0.000 |
| 200                   | -6.60                      | -0.09                                                | -0.09 | -0.0                       | -0.09                                                | -0.000 |
| 220                   | -7.20                      | -0.10                                                | -0.10 | -0.0                       | -0.10                                                | -0.000 |
| 240                   | -7.80                      | -0.11                                                | -0.11 | -0.0                       | -0.11                                                | -0.000 |

TABLE 24

TIME, CONCENTRATION AND RATE DATA AT 104.5° C FOR 34-9700 PEEK

| Time<br>in<br>Minutes | Sole<br>Reaction<br>Excess A | $(-dA/dt) \times 10^3$ |       | Sole<br>Reaction<br>Excess B | $(-dB/dt) \times 10^3$ |       |
|-----------------------|------------------------------|------------------------|-------|------------------------------|------------------------|-------|
|                       |                              | VI-3                   | VI-3  |                              | VI-3                   | VI-3  |
| 0                     | -0.07                        | -7.49                  | 1.375 | .74                          | 2.300                  | 2.128 |
| 20                    | -1.04                        | -6.04                  | .868  | .62                          | 2.045                  | 2.073 |
| 40                    | -1.13                        | -4.43                  | .643  | .57                          | 1.845                  | 2.203 |
| 72                    | -1.12                        | -3.66                  | .510  | .44                          | 1.626                  | 2.366 |
| 104                   | -1.46                        | -2.77                  | .418  | .35                          | 1.388                  | 2.503 |
| 140                   | -1.25                        | -2.04                  | .323  | .443                         | 1.070                  | 1.754 |
| 180                   | -1.14                        | -1.67                  | .264  | .303                         | 1.074                  | 1.456 |
| 240                   | .19                          | .323                   | .150  | .108                         | 1.079                  | .851  |

TABLE III  
 TIME, DISCOMMITMENT AND RISES DATA AT 200° E FOR 33-35 YEARS

| Time<br>in<br>minutes | Solar<br>position<br>angle $\lambda$<br>$^\circ$ -3 | $\frac{I - I_0(\cos \lambda)}{I_0 - I}$<br>$10^{-3}$ | $\frac{I - I_0(\cos \lambda)}{I_0 - I}$<br>$10^{-3}$ | Solar<br>position<br>angle $\lambda$<br>$^\circ$ -3 | $\frac{I - I_0(\cos \lambda)}{I_0 - I}$<br>$10^{-3}$ |
|-----------------------|-----------------------------------------------------|------------------------------------------------------|------------------------------------------------------|-----------------------------------------------------|------------------------------------------------------|
| 0                     | 0.00                                                | 1.150                                                | 1.024                                                | 0.00                                                | 0.104                                                |
| 20                    | -1.00                                               | -0.019                                               | 1.137                                                | -0.00                                               | 0.080                                                |
| 40                    | -2.00                                               | -0.440                                               | 1.113                                                | -0.00                                               | 0.052                                                |
| 60                    | -3.00                                               | -0.910                                               | 1.084                                                | -0.00                                               | 0.014                                                |
| 80                    | -4.00                                               | -1.418                                               | -0.002                                               | -0.00                                               | 0.007                                                |
| 100                   | -5.00                                               | -1.959                                               | -0.026                                               | -0.00                                               | 0.003                                                |
| 120                   | -6.00                                               | -2.534                                               | -0.114                                               | -0.00                                               | 0.100                                                |
| 140                   | -7.00                                               | -3.146                                               | -0.260                                               | -0.00                                               | 1.000                                                |
| 160                   | -8.00                                               | -3.793                                               | -0.471                                               | -0.00                                               | 1.999                                                |
| 180                   | -9.00                                               | -4.477                                               | -0.743                                               | -0.00                                               | 1.000                                                |
| 200                   | -10.00                                              | -5.197                                               | -1.083                                               | -0.00                                               | 0.001                                                |

## CHAPTER VII

### DISCUSSION OF RESULTS

The isomers of allyl-oxolene were prepared from the vapor-phase pyrolysis of alpha-pinene. A thorough and extensive investigation into the conditions of preparation of allyl-oxolene did not yield any evidence at all that there are any more than two isomers. A sample of a third isomer isolated by Small (28) was analyzed chromatographically and disclosed it to be a mixture of the two forms A and B, as mentioned before.

The results from the vapor and liquid phase pyrolysis of alpha-pinene confirm previous studies (17, 28) that oxolene is the precursor of allyl-oxolene. Furthermore, these results appear to have clarified the mechanism of formation of the isomers. Although it was noted in previous work that different proportions of the two isomers were produced at various temperatures, it was not known that isomer A is first formed and then isomerizes reversibly into the B isomer. Thus it is possible to prepare at low pyrolysis temperatures, a mixture containing isomer A, but form B must be separated from a mixture of the two isomers.

The two isomers of allyl-oxolene are differentiated by means of their physical constants. Form A has a lower

melting point, lower refractive index, lower density, lower dielectric constant and lower dipole moment than form II. Isomer I has a more complex infrared spectrum than II. The characteristic spectra of the two isomers indicate that isomer I absorbs at a higher wavelength than II. The absorption properties of stereoisomers thus differ with regard to both wavelength of the absorption band and its intensity. Hence the isomers must differ in the spatial arrangement of groups about a plane. If one of the isomers approaches coplanarity (or maximal elongation) it should exhibit a higher degree of resonance and absorb at somewhat longer wavelengths and more intensity. The more symmetrical isomer has fewer bands in the infrared spectrum.

On the basis of the above considerations, structure I, Figure 2, may be assigned to isomer I, while structure II may be assigned to isomer II. Form I should have a smaller dipole moment than form II, and this conclusion is verified by the measured experimental values. Elder (16) synthesized two isomeric dihydroic acids from the two isomers of allyl-oxime, and from the chemical properties concluded that the configurations were as shown above. Reptfield (10) made the same assignment with regard to structure from the Raman spectra of the two forms.

In evaluating the dipole moment, Nagami's relation,  $\epsilon = n^2$ , was used as a first practical criterion of non-polarity. If the dipole moment is zero, the orientation polarization does not contribute to the total polarization which is then equal to the sum of the electronic and atomic polarizations, which are about equal to the molar refraction. At 20° C the differences  $\epsilon - n^2$  for lauric A and B is .1375 and .1661; at 30° C the differences is .1654 and .1645 respectively. From these results it is possible to say that lauric B will have a higher dipole moment.

Thomas (16) determined the dipole moment of allicolones at 20° C, but did not differentiate between the two isomers. The sample he used had the physical constants:  $n_D^{20}$  1.4438,  $d_4^{20}$  .8009,  $\alpha$  2.5974 and  $p$  .43 degree units. The values at 20° C found in this work for lauric A were:  $n_D$  1.5413,  $d_4$  .8688,  $\alpha$  2.4971 and  $p$  .535 d.u. It would therefore appear that Thomas used a sample of allicolones rich in lauric A.

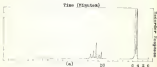
The dipole moments for the two isomeric species were also calculated by means of the Kirkwood equation (12) with the constants for the pure liquids.

$$\mu = .8130 \times 10^{-18} \left[ \frac{RT}{2} \left( \frac{\epsilon - 1}{n^2} \frac{(\epsilon + 1)(2\epsilon + 1)}{3} - \frac{(\frac{\epsilon}{n^2} - 1)}{(\frac{\epsilon}{n^2} + 2)} \right) \right]^{\frac{1}{2}} \quad \text{VII-4}$$

The calculated values at  $25^\circ \text{C}$  were  $\mu = .438$  for isomer A and  $\mu = .407$  for isomer B. The discrepancy between the above values and those obtained from the solution moments was about .1, which can be of the same magnitude as the difference between the solution moment values and the gas moment values. Therefore, for terpene compounds, a good approximate value of the dipole moment may be calculated from the constants of the pure liquid and equation VII-1, dispensing with the method of dilute solutions.

The liquid phase isomerization of allyl-substituted polymers which have a boiling point range of  $170-25^\circ \text{C}$  at 10 mm. Molecular weight determinations of the polymer mixtures, at the early stages of the reaction, indicated that most of it is dimer. Furthermore, the evidence from the ultraviolet spectra suggests that the polymer is a mixture of several dimers. Some of the reacted tubes used in the kinetic runs were sent to Dr. E. Kohl of the Hilsen Co., for analysis with a high resolution gas spectrometer. Typical results are shown in Figure 34, and it is evident from the chromatogram that at least six dimers are present. Furthermore, different dimers are formed according as pure A, pure B or a mixture of A and B is used as the starting material. Five dimers are formed from isomer A, three from B and six from A + B in the early part of the reaction.

Retention Times. Alko-oximes A and B: 4-6 minutes.  
 Dimers: 15-20 minutes.



Retention Times. Alko-oximes A and B: 10-14 minutes.  
 Dimers: 40-60 minutes.



FIGURE 24. Chromatograms Showing All Components of  
 an Alko-oxime A - B Mixture Heated for 2 Hours,  
 Eluted from 25-75. (a) .51 on a 100 ft Capillary  
 column 1 Column at 250° C (b) .51 on a 100 ft Capillary  
 column 1 Column at 200° C for Dimers and 250° C for Polymers.

The first step in treating the kinetic data was to use the experimental reaction velocities to find approximate values for the rate constants of the reversible ~~high-*temperature*~~ isomerization of olefins, that is for the following process:



Since the isomerization was studied in the liquid phase in which complicating side-reactions occur, a special treatment was applied to explain the behavior of the system. Some experimentally obtained conditions permitted considerable simplification of the derived differential equations.

Let  $A$ ,  $B$ ,  $B_1$  ( $i=1, \dots, s$ ) be the concentrations, in mole fraction units, of isomer  $A$ , isomer  $B$  and diene $_i$ , and

$$-dA/dt = u \quad \text{VII-4}$$

$$-dB/dt = v \quad \text{VII-5}$$

Then if  $\log u$  or  $\log v$  is plotted against  $\log A$  or  $\log B$ , some time one straight line is obtained indicating, as expected, that there were complicating features in the reaction. If several dienes are produced from  $AB$ ,  $AB$  and  $A = B$ , then  $u$  and  $v$  are functions of  $A$ ,  $B$  and  $B_1, \dots, B_s$  or

$$u = f_1(A, B, B_1, \dots, B_s) \quad \text{VII-6}$$

$$v = f_2(A, B, B_1, \dots, B_s) \quad \text{VII-7}$$

In complex reactions, the initial rate is of great importance, as it is only at  $t = 0$  that the components of the system are known with any certainty. As  $t \rightarrow 0$ , then  $i \rightarrow i_0$ ,  $E \rightarrow E_0$ ,  $B_1 \rightarrow 0$ ,  $u \rightarrow u_0$  and  $v \rightarrow v_0$ . Thus at  $t=0$ ,

$$u_0 = F_1^0(i_0, E_0) \quad \text{VII-7}$$

$$v_0 = F_2^0(i_0, E_0) \quad \text{VII-8}$$

where  $u_0$  and  $v_0$  are the initial rates,  $i_0$  and  $E_0$  being the initial concentrations. For the reaction velocities  $-di/dt$ ,  $ds/dt$ , the rate equations become:

$$u_0 = k_1 i_0 - k_2 B_1 + F(i_0, E_0) \quad \text{VII-9}$$

$$v_0 = k_2 B_1 - k_3 i_0 + F'(i_0, E_0) \quad \text{VII-10}$$

If the functions  $F$  and  $F'$  are negligible, then as a first approximation, when starting with pure  $i$  or  $E$ , the equations can be simplified to:

$$u_0 = k_1 i_0 \quad \text{VII-11}$$

$$v_0 = k_2 E_0 \quad \text{VII-12}$$

Equations VII-11 and VII-12 would be exact under two conditions. First, if  $E_0$  in VII-9, and  $i_0$  in VII-10 were zero. Second, if the curves for diene formation approached the origin with zero slope. Taking logarithms in VII-11 and VII-12,

$$\log u_0 = \log k_1 + \log i_0 \quad \text{VII-13}$$

$$\log v_0 = \log k_2 + \log E_0 \quad \text{VII-14}$$

According to VII-13 and VII-14, if the  $\log$  of the initial rate is plotted against the  $\log$  of initial concentration, a straight line with unit slope should result. The intercepts, at  $\log A_0$  or  $\log B_0$  equal zero, are the logarithms of the rate constants. Plots of the logarithms of initial rates against the logarithms of initial concentrations are given in Figures 15 and 16. The slopes of these lines are close to unity: 1.1, 1.04, 1.07, 1.06 respectively at 200.0, 200, 204.5 and 225° C for  $\log v_0$  versus  $\log A_0$ ; 1.1, 1.0, 1.0, 1.0 respectively at the same temperatures for  $\log v_0$  versus  $\log B_0$ . The rate constants  $k_1$  and  $k_2$  were calculated from the intercepts of these lines, also by solving simultaneously equations VII-6 and VII-18, solving  $P = P^* + v$ , and using the initial rates from VI-6. The values of the constants are given in Table 10.

If one starts with pure dimer A, it is assumed that

$$A \xrightarrow{k_1} B \quad \text{VII-19}$$

$$AB \xrightleftharpoons[k_4]{k_2} A_2 \quad \text{VII-20}$$

$$A \rightleftharpoons B \xrightleftharpoons[k_3]{k_2} AB \quad \text{VII-21}$$

are the main processes occurring, then

$$A = B + A_2 + AB = 1 \quad \text{VII-22}$$



FIGURE 10. Influence of Temperature on Initial Rate  $\log -d\alpha/dt$  for Chloride Ions Starting with Pure Solvent A.



FIGURE 26. Influence of temperature on initial rate  $r_0 = -dS/dt$  for D-glucose from fermenting with pure B.

TABLE 30  
RATE CONSTANTS FOR HYDROLYTIC  
DECOMPOSITION OF ALK-OCTOATE

| Temperature<br>° C | $k_2 \times 10^3$       |                                     | $k_3 \times 10^3$       |                                     | $k_2/k_3$ |
|--------------------|-------------------------|-------------------------------------|-------------------------|-------------------------------------|-----------|
|                    | From<br>Inter-<br>cepts | From<br>Equations<br>VI-8,<br>VI-10 | From<br>Inter-<br>cepts | From<br>Equations<br>VI-8,<br>VI-10 |           |
|                    |                         |                                     |                         |                                     |           |
| 166.5              | 8.400                   | 2.440                               | 1.400                   | 1.870                               | 1.28      |
| 200.5              | 8.880                   | 2.900                               | 2.880                   | 8.760                               | 1.00      |
| 204.5              | 2.880                   | 8.640                               | 8.360                   | 2.18                                | 1.12      |
| 220                | 8.320                   | 8.380                               | 4.36                    | 4.40                                | 1.48      |

$$-dA/dt = k_1 A + 2k_2 A^2 = k_2(A+B)(B) = k_2 B^2 \quad \text{VII-18}$$

$$-dB/dt = k_2 B + k_2(A+B)(B) = k_1 A \quad \text{VII-19}$$

The rates defined by  $k_1$  and  $k_2$  have been called since these dissociation rates are exceedingly small. Concentration is expressed in mole fraction units, hence VII-18 applies. When  $A$  and  $B$  are kept in a product, each is placed in parenthesis to avoid confusing it with  $AB$ , the symbol for a dimer. It is experimentally observed that after a short period,

$$-dA/dt = 0 \quad \text{VII-21}$$

Inserting condition VII-21 in VII-18 and VII-19, the following equation is obtained:

$$-dA/dt = 2k_2(A)(B) = 2k_2 A^2 \quad \text{VII-22}$$

Equation VII-22 can be integrated to give,

$$\ln \frac{(k_2 B_0 / k_1 + k_2) A}{(k_2 B_0 / k_1 + 1) A_0} = -2k_2 B_0 (t - t_0) \quad \text{VII-23}$$

where  $t_0$  is the time at which condition VII-21 becomes applicable and  $B_0$ ,  $A_0$  are the corresponding concentrations of  $A$  and  $B$  at that time. From VII-22 and VI-21,

$$k_2 = (k_1/t_0 + k_2/t_0) \quad \text{VII-24}$$

Equation VII-23 may be solved for  $k_2$ ,

$$k_2 = \frac{k_1 B_0}{A - A_0} \frac{(\ln_2 e^{-2k_1 B_0 (t - t_0)} + 1)}{(1 - e^{-2k_1 B_0 (t - t_0)})} \quad \text{VII-25}$$

Starting with pure B, the equation

$$2k_1 \frac{b_1^2}{b_2^2} = k_2 \quad \text{VII-26}$$

may be substituted for VII-18, and another set of equations similar to VII-24 and VII-25 can be obtained for  $k_1^2$  and  $k_2$ . The constants  $k_1$ ,  $k_1^2$  and  $k_2$  were calculated at each temperature. Constant  $k_2$  found from equation VII-26 differed by about a factor of two from that found from the equation applicable when A is the starting material. At each temperature there was appreciable drift in the constants. Arrhenius plots for  $k_1$  and  $k_1^2$  showed a slight negative drift, indicating either that the slope was zero or that the activation energy was negative, a physical impossibility. Arrhenius plots for  $k_2$  were normal.

It was thus necessary to find other equations compatible with the postulated mechanism and the experimental results. If the reactions represented by equations VII-14 and VII-20 are subsidiary ones then starting with pure A or pure B, and applying the additional condition (for runs with B)

$$-dA/dt = 0 \quad \text{VII-27}$$

the following relationships may be derived. For runs starting with A,

$$-dA/dt = k_1 A + k_2 B + k_3(A)(B) \quad \text{VII-28}$$

and for runs with  $B_2$

$$-dH/dt = k_2B = k_2B_0(1 - \alpha_2)(13) \quad (VII-20)$$

Applying VII-21 and VII-27 to VII-20 and VII-22 and integrating, the following equations are obtained:

$$\log k_2/\alpha = [k_2 B_0 (1 - \alpha_2)]/(4.605) \quad (VII-23)$$

$$\log k_2/\beta = [k_2 B_0 (1 - \alpha_2)]/(4.605) \quad (VII-24)$$

From VII-23 and VII-24 expressions for  $k_2$  can be obtained:

$$k_2 = \frac{(4.605)(\log k_2/\alpha)}{B_0(1 - \alpha_2)} \quad (VII-25)$$

$$k_2 = \frac{(4.605)(\log k_2/\beta)}{B_0(1 - \alpha_2)} \quad (VII-26)$$

The values of  $k_2$  calculated from the above equations are given in Tables 27 and 28. Arrhenius plots for the  $k_2$  constants are shown in Figure 27. They have almost identical slopes, and the activation energy was found to be 14.2 kcal/mole. The  $k_2$  constants define a bimolecular association involving, perhaps, a 1:1 addition of an alcohol to a triacidic system, that is a Mann-Ritter reaction. Experimental activation energies for this type of reaction have been reported as from 10 to 22 kcal/mole (34). Arrhenius plots for  $k_1$  and  $k_3$  in Table 28 yield activation energies of 20.1 and 22.4 kcal/mole respectively. Experimental activation energies for acid-catalyzed isomerizations range between 10 and 20 kcal/mole (34).

TABLE IV  
RATE CONSTANT  $k_p$  VALUES FROM EQUATION VII-35  
FOR RIMS WITH B AS THE WRAPPING MATERIAL

| Time<br>(minutes) | $k_p \times 10^3$      |                        |                        |                        |
|-------------------|------------------------|------------------------|------------------------|------------------------|
|                   | $200.0^\circ \text{C}$ | $220.0^\circ \text{C}$ | $234.0^\circ \text{C}$ | $250.0^\circ \text{C}$ |
| 60                | —                      | 38.88                  | 46.00                  | 55.00                  |
| 70                | 36.80                  | 46.00                  | 46.75                  | 55.00                  |
| 84                | 36.80                  | 38.00                  | 46.40                  | 55.00                  |
| 98                | 36.80                  | 46.74                  | 42.50                  | 55.75                  |
| 106               | 35.80                  | 46.80                  | 47.00                  | 55.00                  |
| 120               | 36.50                  | 46.80                  | 46.50                  | 56.20                  |
| 130               | —                      | 46.81                  | 46.00                  | —                      |
| 144               | —                      | 46.80                  | 45.00                  | —                      |
| 150               | —                      | 46.80                  | 46.00                  | —                      |
| 160               | —                      | 38.80                  | —                      | —                      |
| 180               | 36.80                  | —                      | 46.00                  | —                      |
| 190               | 35.80                  | —                      | —                      | —                      |
| 210               | 36.80                  | —                      | —                      | —                      |
| 240               | 36.50                  | —                      | —                      | —                      |
| Average           | 36.64                  | 45.32                  | 46.42                  | 55.00                  |

TABLE 34

SAFETY COEFFICIENT  $k_s$  VALUES FROM EQUATION VII-38  
FOR ROAD WITH 4 LB PER SQUARE INCH

| Time<br>(minutes) | $k_s \times 10^3$ |           |           |           |
|-------------------|-------------------|-----------|-----------|-----------|
|                   | 100,000 c         | 200,000 c | 300,000 c | 400,000 c |
| 30                | —                 | 33.33     | 33.33     | 33.33     |
| 75                | 33.33             | 33.33     | 33.33     | 33.33     |
| 150               | 33.33             | 33.33     | 33.33     | 33.33     |
| 300               | 33.33             | 33.33     | 33.33     | 33.33     |
| 450               | —                 | 33.33     | —         | —         |
| 600               | 33.33             | —         | —         | —         |
| STOPPAGE          | 33.33             | 33.33     | 33.33     | 33.33     |

- (a)  $k_2$  from 1971-83  
 (b)  $k_2$  from 1971-83



FIGURE 10. Relationship between  $k_2$  and  $k_1$ .

Values for  $k_1$  and  $k_2$  were obtained quite independently of initial rates, by solving simultaneously equations VII-26 and VII-27.

$$k_1 = \frac{(-dA/dt - k_2A_1B_1)(B_2) + (-dA/dt - k_2A_2B_2)(B_1)}{(A_1B_2 - A_2B_1)} \quad \text{VII-26}$$

$$k_2 = \frac{(-dA/dt - k_1A_1B_1)(A_2) + (-dA/dt - k_1A_2B_2)(A_1)}{(A_1B_2 - A_2B_1)} \quad \text{VII-27}$$

where  $-dA/dt$ ,  $A_1$ ,  $B_1$  are the rates and concentrations from runs starting with pure  $A$ , while  $-dA/dt$ ,  $A_2$ ,  $B_2$  are the values from  $B$  runs. The values of  $k_1$  and  $k_2$  given in Table 20 were calculated from equations VII-26 and VII-27 with the rates from equation VI-5 and the corresponding concentrations at 60 and 180 minutes respectively for each temperature. Arrhenius plots are shown in Figures 28 and the activation energies for  $k_1$  and  $k_2$  are 26.4 and 13.2 kcal/mole respectively.

The integrated equations VII-26 and VII-27 were used with the experimental time-concentration values. The following empirical relationships were also derived by a trial and error process and the use of the observed peak-concentration values.

$$-dA/dt = k_2(A_2)^{1/2}(A)^{1/2} \quad \text{VII-28}$$

$$-dA/dt = k_1(A_2)^{1/2}(A)^{1/2} \quad \text{VII-29}$$

The constants  $k_2$  found from equations VII-28 and VII-29

TABLE 29  
RATE CONSTANTS  $k_1$  AND  $k_2$   
FROM EQUATIONS VII-24 AND VII-25

| Temperature $^{\circ}\text{C}$ | $k_1 \times 10^3$ | $k_2 \times 10^3$ |
|--------------------------------|-------------------|-------------------|
| 188.5                          | 1.85              | 1.05              |
| 200                            | 2.13              | 1.08              |
| 206.5                          | 2.40              | 1.71              |
| 210                            | 2.50              | 1.86              |



FIGURE 20. Arrhenius Plots for Rate Constants  $k_1$  and  $k_2$ .

are given in Table 4b. An Arrhenius plot for these  $R_p$  values is given in Figure 8b. The activation energy of 29.8 kcal/mole is almost the same as that found from the  $k_p$  values.

Any mechanism from which VII-26 and VII-27 can be derived necessitates the involvement of free radicals. The possibility cannot be ruled out completely that a systematic error was introduced in the DSC calculation of rates to account for the square-root dependency, particularly in the form of VII-26 and VII-27 is as similar to that derived from VII-28 and VII-29. Nevertheless, in a system containing unsaturated molecules, the thermal production of free radicals is very probable (28,29).

The rate of disappearance of a monomer in a free radical polymerization reaction (28) can be represented by the equation,

$$-dM/dt = k_p(R_p/k_t)^{1/2}(M) \quad \text{VII-30}$$

where  $M$  is a monomer,  $R_p$  the specific rate of radical production,  $k_p$  the rate constant for the propagation reaction, and  $k_t$  the rate constant for the termination reaction. Equation VII-30 would reduce to VII-26 if  $R_p = k_1(k_2/k_3)^{1/2}$  and  $k_p/k_t^{1/2} = R_p$ .

A summary of the constants found for the isomerization and elimination of allyl-oxirane is given in Table 4b. The  $\log$  of the frequency factor,  $\log A$ , was also calculated

TABLE 40  
CONSTANT  $k_d$  AT  $100.0^\circ \text{C}$

| Time<br>(Minutes) | $k_d \times 10^3$       |                         |
|-------------------|-------------------------|-------------------------|
|                   | From Equation<br>VII-26 | From Equation<br>VII-27 |
| 20                | 7.00                    | 7.41                    |
| 30                | 7.00                    | 7.08                    |
| 100               | 7.00                    | 7.44                    |
| 120               | 6.80                    | 7.00                    |
| 180               | 6.80                    | 7.00                    |
| 210               | 6.77                    | 7.00                    |
| 240               | 6.80                    | 6.80                    |
| Average           | 6.83                    | 7.00                    |

CONSTANT  $k_d$  AT  $104.0^\circ \text{C}$

|         |       |       |
|---------|-------|-------|
| 20      | 9.008 | 10.00 |
| 30      | 9.00  | 10.07 |
| 100     | 10.04 | 10.00 |
| 120     | 9.00  | 10.00 |
| 180     | 9.00  | 10.10 |
| 240     | 9.00  | 10.10 |
| Average | 9.28  | 10.01 |

CONSTANT  $k_d$  AT  $104.0^\circ \text{C}$

|         |       |       |
|---------|-------|-------|
| 40      | 11.44 | 11.01 |
| 50      | 11.40 | 11.07 |
| 60      | 11.74 | 11.00 |
| 100     | 11.71 | 11.00 |
| 180     | 11.40 | 11.44 |
| 200     | 10.97 | 11.01 |
| Average | 11.40 | 11.00 |

CONSTANT  $k_d$  AT  $110^\circ \text{C}$

|         |       |       |
|---------|-------|-------|
| 30      | 13.00 | 17.00 |
| 50      | 13.30 | 17.74 |
| 60      | 13.00 | 17.00 |
| 80      | 13.00 | 17.00 |
| 70      | 13.00 | 17.00 |
| 90      | 13.14 | 17.00 |
| Average | 13.30 | 17.00 |

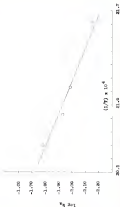


FIGURE 10. Arrhenius Plot for Rate Constant  $k_2$   
from Equations (11-8) and (11-9).

TABLE 42

RESULTS OF EXPERIMENTS FOR MASS-TRANSFER CHARACTERISTICS AND SOLUBILITIES

| Temperature<br>$T_g$ | $(C_1/h) \times 10^{-4}$ | $k_1 \times 10^3$<br>From<br>Fig. 34 | $k_2 \times 10^3$<br>From<br>Fig. 35 | $k_3 \times 10^3$ |                 | $k_4 \times 10^3$<br>From<br>Fig. 36,<br>Fig. 37 |
|----------------------|--------------------------|--------------------------------------|--------------------------------------|-------------------|-----------------|--------------------------------------------------|
|                      |                          |                                      |                                      | From<br>Fig. 38   | From<br>Fig. 39 |                                                  |
| 144.5                | 21-51.6                  | 1.40                                 | 1.20                                 | 50.38             | 80.44           | 7.12                                             |
| 80.0                 | 21-123                   | 8.12                                 | 8.02                                 | 20.40             | 40.50           | 15.14                                            |
| 804.5                | 20-624                   | 2.45                                 | 8.71                                 | 16.42             | 46.42           | 11.51                                            |
| 212                  | 58-685                   | 2.80                                 | 2.86                                 | 45.07             | 60.05           | 14.20                                            |

| SOLUBILITY DATA, mol./mol. |       |                       |                       |
|----------------------------|-------|-----------------------|-----------------------|
| $k_1$                      | $k_2$ | $k_3$ from<br>Fig. 38 | $k_4$ from<br>Fig. 39 |
| 21.4                       | 14.4  | 14.2                  | 14.2                  |

and for  $k_1$  and  $k_2$   $\log a$  (in terms of seconds) is 14.8 and 13.7 respectively which are normal for unimolecular reactions. For  $k_3$  and  $k_4$  the values of  $\log a$  (in terms of minutes) are 8.8 and 10.3, which are also normal for a second order reaction, presumably the dimer formation.

The constancy of rate constants over a given concentration range is usually taken as a sufficient criterion for the plausibility of a postulated mechanism. However, although this condition is necessary, it is by no means sufficient. A further test was applied to the mechanism from which equations VII-28 and VII-29 were derived. It was found that if the rates are calculated with VII-28, 29 and the appropriate constants ( $k_1$ ,  $k_2$  and  $k_3$ ), they are close to the observed ones. For example, for runs starting with A at 185.7° C. and 4-55, 60 and 100 minutes the calculated rates,  $\times 10^3$ , are 2.5, 2.60 and 1.80. The observed rates,  $\times 10^3$ , are: 2.37 or 2.38 (equations VI-2 or VI-3), 2.08 or 2.05, and 1.64 or 1.72 respectively. For runs starting with B at 185.5° C. and 1-66, 60 and 100 minutes, the calculated rates,  $\times 10^3$ , are 2.05, 1.83 and 1.53. The observed rates,  $\times 10^3$ , are 2.08, 1.80 and 1.43 respectively. For mixtures of A + B the observed rates are much smaller than the calculated ones. However, if the  $k_4$  value is substituted for  $k_3$ , the calculated rates are then in line with the observed ones.

at 180-170, the rates,  $-d\bar{M}_n/dt$ , calculated for a mixture 1 + 3 as the starting material, with the  $k_p$  constant, at 4-50, 60 and 100 minutes, are:  $1.55 \pm 10^{-3}$ ,  $1.40 \pm 10^{-3}$ ,  $.745 \pm 10^{-3}$ ; the observed rates are:  $1.40 \pm 10^{-3}$ ,  $1.35 \pm 10^{-3}$ ,  $.58 \pm 10^{-3}$ . The calculated rates,  $-d\bar{M}_w/dt$ , for the same mixture are:  $1.55 \pm 10^{-3}$ ,  $1.54 \pm 10^{-3}$ ,  $.58 \pm 10^{-3}$ ; the observed rates are:  $.54 \pm 10^{-3}$ ,  $.50 \pm 10^{-3}$ ,  $.58 \pm 10^{-3}$ .

There are probably several reasons why the assumed mechanism is not applicable beyond about 50 percent of the reaction. First, it is known that molecular constants change with a decrease of the reagent concentrations. Second, a greater and greater uncertainty may be introduced in the calculation of concentrations from the chromatograms as the reaction proceeds. It will be recalled that a constant volume, one microliter, was used for all analyses, and with the increase of diene content the chromatogram area becomes smaller. Third, it was observed that the diene from the early stages of the reaction absorbed at 240 m $\mu$ , which is due to a diene chromophore. Thus the diene may be a mixture containing species with cyclohexene or cyclohexadiene rings. The absorption decreases sharply during the later stage of the reaction. About 80 percent of the diene with the diene chromophore disappear on heating for 84 hours. Hence it is possible that polymerization may

occur at the later stage of the reaction. This would happen if the terminal carbon bonds reacted.

## CHAPTER VIII

### SUMMARY

The pyrolysis of alpha-pinene, both in the vapor and liquid phases was studied with a view to elucidating the mechanism of formation of the isomers and dimers of alpha-silene.

The isomerization products of alpha-pinene, both in the vapor and liquid phases, have been identified and separated.

Very pure samples of the two isomeric forms of alpha-silene were prepared from the vapor phase pyrolysis of alpha-pinene. The isomers were separated by efficient fractionation columns and further purified by fractional crystallization.

Some physical properties were determined. On the basis of these the structure of  $\text{C}_{10}\text{H}_{16}\text{C}-\text{C}-\text{C}_4\text{H}_8$ ,  $\text{C}_{10}\text{H}_{16}\text{C}-\text{C}-\text{C}_4\text{H}_7$  was assigned to Isomer A and  $\text{C}_{10}\text{H}_{16}\text{C}-\text{C}-\text{C}_4\text{H}_8$ ,  $\text{C}_{10}\text{H}_{16}\text{C}-\text{C}-\text{C}_4\text{H}_7$  to Isomer B.

The evidence presented here indicates that Isomer A is formed at all temperatures and that it is reversibly converted to Isomer B. At high temperatures, an equilibrium is established between the two forms, so that it is not possible to obtain Isomer B only either from A or from alpha-pinene.

The reversible isomerization of allyl-oxirane was studied in the liquid phase. The reaction is a complex one, possibly involving a free radical mechanism. An attempt was made to work out the simple unimolecular reaction,



from the complex one involving the formation of as many as six dimers when A is the starting material. The activation energies and frequency factors were obtained and are of the correct order of magnitude for unimolecular and bimolecular reactions (reversible isomerization and dimer formation).

From the evidence and data obtained in this work, together with results of previous studies, the over-all reaction of allyl-oxirane formation now appears to be:



There is also evidence for over extensive polymerization occurring in the liquid phase when allyl-oxirane is heated for a prolonged period of time.

The study of the isomerization process indicated by equation VIII-1 in the vapor phase should permit a direct determination of the first order kinetic data.

# BIBLIOGRAPHY

1. C. Sauerb, and V. Langer, *Bull. Soc. Chim. P.*, 488-89 (1908) *Sub. 30*, 2077<sub>7</sub> (1907).
2. C. J. Wehner, *Ind. Eng. Chem. 30*, 127-29 (1907); *Sub. 1*, 2137<sub>9</sub>.
3. C. J. Wehner, *Chem. Weekblad 4*, 222 (1907); *Chemisches Zentralblatt 31*, 62 (1907).
4. C. J. Wehner, *Ind. Eng. Chem. 27*, 493 (1905); *Sub. 1*, 504.
5. C. J. Wehner, *Ind. Eng. Chem. 27*, 443-44 (1905); *Sub. 2*, 1037.
6. C. J. Wehner, *Ind. Eng. Chem. 20*, 252-55 (1917); *Sub. 11*, 2084.
7. F. O. Fischer and E. Langer, *Ber. Berl. Chem. Ges.*, 37B, 493-74 (1903).
8. H. Langer, *Bull. Soc. Chim. P.*, 516-21 (1902).
9. E. A. Arrows, *Ber. Berl. Chem. Ges.*, 37B, 263-3 (1904).
10. E. A. Arrows, *Ber. Berl. Chem. Ges.*, 37B, 1846 (1904).
11. E. A. Arrows, *J. Ind. Eng. (C.S.E.S.I.)*, 2, 206-25 (1905).
12. E. A. Schmitt and E. Pollin, *J. Am. Chem. Soc.*, 32, 2017-22 (1910).
13. F. H. Smith and E. A. Schmitt, *J. Am. Chem. Soc.*, 37, 2027-32 (1915).
14. F. H. Smith and E. A. Schmitt, U. S. Patent No. 9, 455, 755, March 21, 1930.
15. E. E. Pagani and F. H. Smith, *J. Am. Chem. Soc.*, 37, Sub-3 (1915).
16. E. E. Pagani and F. H. Smith, *J. Am. Chem. Soc.*, 33, 828-32 (1911).

17. J. E. Seebins and E. C. Cook, and P. E. Pappas, unpublished.
18. T. N. Siskin, *J. Gen. Chem. (U.S.S.R.)*, **12**, 1642-48 (1946) (in Russian).
19. T. N. Siskin, *J. Gen. Chem. (U.S.S.R.)*, **12**, 1479-86 (1946) (in Russian).
20. T. N. Siskin, *J. Applied Chem. (U.S.S.R.)*, **18**, 890-2 (1946) (in Russian).
21. T. N. Siskin, *J. Gen. Chem. (U.S.S.R.)*, **18**, 809-810, 879-80 (1946) (in Russian).
22. E. I. Burwell, *J. Am. Chem. Soc.*, **73**, 4461 (1951).
23. E. C. Cook, Dissertation, Department of Chemistry, University of Florida, 1950.
24. J. E. Seebins and E. C. Cook, *J. Am. Chem. Soc.*, **73**, 4778 (1951).
25. P. G. Rice and G. E. Rice, "The Aliphatic Free Radicals," The John Hopkins Press, Baltimore, Md. (1938).
26. J. E. Seebins and P. E. Pappas, *J. Phys. Chem.*, **65**, 1631 (1961).
27. J. T. Smith, Thesis, Department of Chemistry, University of Florida, 1953.
28. J. L. Wiseman and H. Cox, "The Terpenes," Vol. 1 (1947).
29. G. Sponck, P. Salas, T. Durand and R. Fieser, *Bull. Soc. Chim. B.*, 338-39 (1958).
30. J. J. Gayfield, R. A. Bell and L. I. Goldstein, *J. Am. Chem. Soc.*, **68**, 121-23 (1946).
31. E. Alfrey, A. Dreize, S. Bywater and T. Siskin, *Jpn. Soc.*, 1-10 (1947).
32. F. Daniels, "Articles of Physical Chemistry," p. 277 (1944).

33. H. S. Rutherford, The Furfural and Furfural Resin Series, 2d, 453-4 (1962).
34. L. I. Bartushev, Russ. Printed. Data (I. Russian Chem.), 21, 546-55 (1945).
35. E. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, New York, N. Y., p. 229 (1950).
36. G. L. Bratschkov, Tsvetl. Anal. Zhuk. (U.S.S.R.), Spectr. Anal. Zhuk., 490-3 (1955); Russ. Chem. Revs.
37. M. D. Stalling, E. E. Fagella and J. E. Hawkins, Ind. Eng. Chem., Anal. Ed., 24, 503 (1952).
38. J. Weinberger, "Techniques of Organic Chemistry," Vol. II, pp. 345-348, 354-356, Interscience Publishers, N. Y. (1955).
39. E. J. Hirschberg and E. R. Andrews, Ind. Eng. Chem., Anal. Ed., 2, 344 (1932).
40. J. E. Hawkins and E. A. Frost Jr., Ind. Eng. Chem., 43, 2012 (1951).
41. E. E. Voth, "Laboratory Techniques in Organic Chemistry," pp. 58-65, McGraw Hill Book Co., N. Y. (1955).
42. J. E. Hawkins and W. L. Harris, J. Exp. Chem., 24, 1587 (1952).
43. H. E. Lipkin, J. A. Davison, W. T. Harvey and E. J. Harris Jr., Ind. Eng. Chem., Anal. Ed., 26, 48 (1954).
44. H. L. Lange, "Handbook of Chemistry," 2d, Vol. 7, p. 1218, Handbook Publishers Inc., Eastbury, Ohio (1946).
45. J. Timmerman, "Physical-Chemical Constants of Organic Compounds," Elsevier Pub. Co., N. Y. (1950).
46. J. Weinberger, "Techniques of Organic Chemistry," Vol. I, Part III, Chapter XXXI, Interscience Publishers, Inc., N. Y. (1955).
47. S. Rutherford, J. Exp. Chem., 22, 485 (1950).

49. I. P. Kulshrewst and W. D. Taylor, *J. Am. Chem. Soc.*, **66**, 2040 (1944).
50. B. N. Eldred, T. D. Barjish and L. J. Goldblatt, *T. S. Peckett Co.*, **8**, 487, 500 September 10, 1947.
51. J. Frost and R. S. Peurson, "Kinetics and Mechanism," John Wiley & Sons Inc., N. Y. (1953).
52. J. L. Hoge, W. Shoup and R. Spring, *J. Am. Chem. Soc.*, **63**, 977 (1941).
53. O. L. Thomas and J. E. Puckner, *J. Am. Chem. Soc.*, **76**, 4960 (1954).
54. C. F. Smith "Dielectric Behavior and Structure," p. 528, McGraw-Hill Book Co. Inc., N. Y. (1955).
55. S. Glasstone, K. L. Laidler and H. Spring, "The Theory of Rate Processes," McGraw-Hill Book Co. Inc., N. Y. (1941).
56. E. W. Ranson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co. Inc., N. Y. (1950).
57. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y. (1953).

### BIOGRAPHICAL SKETCH

Demetrios Cappel was born in Cairo, Egypt on March 14, 1908. He attended Arab High School there and graduated in June, 1926. He attended Berea College, Berea, Kentucky, receiving the degree of Bachelor of Arts in Chemistry in 1930.

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This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February 3, 1900

  
Dean, College of Arts and Sciences

\_\_\_\_\_  
Dean, Graduate School

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